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A User's Guide for REDEQL.EPA A Computer Program for Chemical Equilibria in Aqueous Systems

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This guide allows one to use the program without reference to the FORTRAN program. The capabilities and limitations of the program are discussed. The formats for input and explanation of output are given with examples illustrating the various program options. Common user errors are discussed.

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A USER'S GUIDE FOR REDEQL.EPA

A Computer Program for Chemical Equilibria in Aqueous Systems

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its fifteen major field installations, one of which is the Corvallis Environmental Research Laboratory (CERL).

The primary mission of the Corvallis laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects, and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes a computer program (REDEQL.EPA) for determining aqueous chemical equilibria among metals and ligands under various conditions of concentration, pH, and oxidation. It represents an update of material presented at a users' workshop at CERL in May, 1974.

A. F. Bartsch
Director, CERL

ABSTRACT

This user's guide explains the use of the computerized chemical equilibrium program REDEQL.EPA. This program computes aqueous equilibria for up to 20 metals and 30 ligands in a system. The metals and ligands are selected from a list of 35 metals and 59 ligands for which thermodynamic data for complexes and solids have been stored in a data file. More data may be added by the user. The equilibria which the program considers include complexation, precipitation, oxidation-reduction, and pH-dependent phenomena.

This guide allows one to use the program without reference to the FORTRAN program. The capabilities and limitations of the program are discussed. The formats for input and explanation of output are given with examples illustrating the various program options. Common user errors are discussed.

This report covers a period from July, 1975 to July, 1977 and work was completed as of September, 1977.

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I. INTRODUCTION

The program described here, REDEQL.EPA, is a modification of REDEQL2 which was developed over a number of years at the California Institute of Technology by Morgan, Morel, and McDuff under grants initially from Gulf Oil Corporation, the Environmental Quality Laboratory of Cal Tech, and the Rockefeller Foundation and, since 1972, under grants from the Environmental Protection Agency. Some information in this guide is taken from W. M. Keck Laboratories Technical Report EQ-73-02 by McDuff and Morel (1).

The purpose of this guide is to make program use as simple as possible. The program capabilities will be illustrated with a series of examples. Emphasis is on defining program input and interpreting output and on how the program can serve the user. No description of the FORTRAN program is included. The method of computation for the program was originally published by Morel and Morgan (2). For complete details of the program consult references 1 and 2.

Applications of the program differ broadly, and there are many unexplored areas to which the program might be applied. The impact of a chemical spill on a water supply can be assessed. For example, what happens when very acidic titanium wastes are dumped in the New York Bight? What is the white material that precipitates? To answer these questions the user needs the analytical concentrations in the dumped material and analytical data for seawater. Total concentrations of metals and ligands when one part of the dumped material is diluted with 100 parts seawater can be used with the computer program to determine the resulting speciation of the chemicals. If solids precipitate, these will be identified. Some other parameters, such as the final pH of the mixture, will also be given. These results can rapidly be compared with results for different dilution.

The program can serve as a quick check of laboratory measurements or give a preview of what will happen in an experiment. Similar results between the program output and laboratory analysis support the validity of the program and the experimentalist's technique. Differing results raise questions such as: "Is what should be measured actually being

measured?" and "If the experimental results are correct, what phenomenon is occurring in solution that the program doesn't take into account?"

While the limitations of the program are stressed in Section II, page 7, it is important to consider why the program might be used in preference to laboratory work. After some practice, using the program is generally faster. It should involve fewer work hours than laboratory work. When many similar situations are to be considered and the validity of the program results for some of these situations has been confirmed in the laboratory, the results for the rest of the situations could be calculated by the program.

Suppose that the pH and mercury concentration in a river are known and a chemical is spilled into that river. To determine the effects on pH and mercury speciation, the program could be run for appropriate mixtures of spilled chemical and river water. For a laboratory simulation experiment, one would need unpreserved samples, but these would be susceptible to mercury loss or pH changes. The program results, however, are unbiased by contamination or loss.

REDEQL.EPA gives information that routine analytical work does not reveal. For instance, it is easy to measure dissolved copper in seawater, but it is difficult to measure that this copper is 68% free ion, 23% chloride complexes, 7% a sulfate complex, and 2% a hydroxide complex. One of these forms might vary greatly in toxicity from another, so that their identity is important. This distribution might be very sensitive to changes in other trace metal or ligand concentrations or pH. The program can be used to vary such concentrations and pH and thus can reveal which variables are most important in controlling the distribution of copper in the aqueous system and need further study.

I-A. DESCRIPTION OF THE PROGRAM CAPABILITIES

This program is designed to compute chemical equilibria involving solids, complexes, oxidation-reduction, and mixed solids in an aqueous system. The adsorption scheme formerly used with REDEQL2 is still intact but not described here because adsorption routines are being modified. These modifications will be reported in a future publication.

Ionic strength may be calculated or specified and formation constants for solids and complexes are computed from the thermodynamic data for infinite dilution and from ionic strength. Interaction capacities and intensities as described by Morel et al. (3) can also be computed.

The primary inputs for the program are the total concentrations of metals and ligands in the system, including quantities in solid and gas phases if these are allowed to interact with the aqueous system. Concentration may be in molar units or milligrams/liter. The thermodynamic data file contains thermodynamic data for metals, ligands, solids, complexes, redox reactions, and mixed solids. It presently includes thermodynamic data for 35 metals and 59 ligands which are listed in Table 1, page 45. More can be added; see Section V-A, page 35. Up to ten cases of different total concentrations for a set of metals and ligands selected from those available can be treated by the program in one run. A maximum of 20 metals and 30 ligands may be included in any one system considered. The results of the program are the speciation of the metals and ligands in various forms and combinations. A large amount of complexation and solubility data is stored for up to three solids and six complexes for each metal-ligand pair. It is possible to allow for supersaturation with respect to any of the possible solids. Data for 24 redox reactions from the thermodynamic data file are listed in Table 2, page 46, and the user may specify which reactions will be included in a particular run. Table 3, page 47, shows six mixed solids, which contain more than one metal or ligand (not including H^+ or OH^-). A complete explanation of the thermodynamic data file and how it may be modified is given in Section V-A, page 35. The mechanics of creating, maintaining, and using one's own thermodynamic data file are given in Section V-B, page 40.

EPA research laboratories and regional offices are served by a national computer services contract, frequently available to non-EPA personnel working cooperatively with EPA. In August, 1977, REDEQL.EPA was available on the COMNET IBM system of the Washington Computer Center. If the system is changed under future contracts, this program will still be available.

The program may be used with either laboratory, field, or hypothetical input data. The results of the program are based on thermodynamic data, which have been previously measured in less complex systems, applied to the input data. If the formation constant for a solid or complex is not in the thermodynamic data file, that solid or complex will not be predicted to form in the aqueous system being studied, even though it may indeed be present. If a chemical (metal or ligand) present in the system is omitted from the input data for the program, then the results will be in error. If the pH of the system is not known or if the redox potential is not known when oxidation or reduction might occur, then results will be in error. pH is not required if the chemical form of all species introduced to the system is known (see Section III-D, page 17).

The program is useful for situations such as 1) mixing compounds together in a beaker of water and predicting what would happen after equilibrium is reached, 2) determining the fate of a chemical introduced into a well-characterized body of water (assuming no further mixing or dilution), 3) predicting removal of chemicals through precipitation under varying conditions of pH, redox potential, and ionic strength, 4) confirming laboratory results for pH or precipitation, 5) predicting pH or metal concentration in aquatic media for biological experiments, 6) examining mixing and dilution effects in sequential cases with varying initial concentrations. There are many situations in which the program's use is limited and these are discussed in Section II, page 7.

I-B. A SIMPLE SYSTEM

A simple aqueous system might contain calcium, sodium, magnesium, iron(III), carbonate, bicarbonate, and chloride ions and combinations thereof. Any aqueous system also has some hydrogen ions, H^+, and hydroxide ions, OH^-. These ions do not exist independently of one another but may form complexes or even solids.

Suppose that 0.5 mole NaCl (29 g), 0.1 mole $CaCO_3$ (10 g), 0.05 mole $Mg(HCO_3)_2$ (4.2g), and 0.01 mole $FeCl_3$ (1.6 g) are placed in a

liter of water. Do all the species exist only as ions in solution or do other things happen? Complexes such as $CaHCO_3^+$ may form. Solids such as $MgCO_3$ or $Fe(OH)_3$ may precipitate from the solution. Fe^{3+} might be reduced to Fe^{2+}. Dolomite, $CaMg(CO_3)_2$, may precipitate. This system will serve as an illustrative example for use of the program.

In Section III, page 10, this example will be used to demonstrate the flexibility of the program, how the initial run is set up, and how the output is interpreted. Variation of some of the input parameters will show other facets of the program. How these changes affect the output will be discussed and illustrated.

It should be stressed that the quantities used to describe an aqueous system do not have to be chemical compounds, as in the example above, but may be analytical concentrations of aqueous ions such as those concentrations that might be available from field data. If analytical data are used it is well to keep the constraint of electroneutrality in mind (see Section II, page 7).

I-C. HOW TO USE THIS GUIDE

A brief overview of the scope of REDEQL.EPA has been given in the introduction. The specific examples which are worked through in Section III can be used as further demonstration of the scope of the program or as models upon which to pattern one's own input data. After reading this introduction the user is advised to read Section II, page 7, on the limitations of the program and to bear these limitations in mind while using the program.

The thermodynamic data are essential to the program. How to obtain a copy of those data is described in Section V-B, page 40. The form in which equilibrium constants are expressed is outlined and exemplified in Section V-C, page 41. The format for storage of these constants and other metal-ligand data is discussed with examples in Section V-A, page 35, and is summarized in Table 6, page 55. All tables are near the end of this guide. Section V-A also includes information on how the thermodynamic data may be changed to include new or different data. The mechanics of creating and using a modified thermodynamic file are given in Section V-B, page 40.

The FORTRAN version of the program is not given here. It may be obtained, without documentation, by the following steps:

(log on to WCC)
PRINT CN.EPABDJ.CPR1.REDEQL.EPA,ROUTE=REMOTENN
where NN is the user's terminal number.

In Section III, page 10, the input required by the program is described and samples given. Table 4, page 48, should be examined in conjunction with Section III. Sample outputs from the input data are shown in figures in the computer printout section at the end of the guide. In individual sections ionic strength, total hydrogen, solids, gas phase, mixed solids, and oxidation-reduction are considered, and particular problems that can arise from variation of parameters under different situations are stressed. When different options are given by the program, e.g. fixed or calculated pH, the description gives some advice on where to use either option. The user should read all those sections which pertain to his system and should not rely only on Table 4, which gives the input format. Some undesired results, e.g. changes in imposed conditions, are difficult to detect without hints as to where to check for them.

Section IV, page 26, is a more complete description of the formats of the output from the program. References to various outputs are given in Table 5, page 54.

II. LIMITATIONS OF REDEQL.EPA

Some problems which arise in the use of REDEQL.EPA are enumerated below. Some of them, such as poor analytical data, are the responsibility of the user. Others such as kinetics of reactions were never intended to be within the scope of the program. Still other limitations may be lifted in the future by refinement of the program or afford no obstacle now for well defined cases. The most serious limitations are:

1. The program is for equilibrium. Kinetics of dissolution, precipitation and oxidation/reduction are not considered. Few natural systems are truly at equilibrium because of slow chemical processes, biological activity, and transport.

2. The program does not consider surface effects. Neither the variation of surface properties of solids from bulk properties nor adsorption is included. Although the program may incorporate adsorption on some solids in the near future, this will be adsorption only for well-characterized surfaces such as metal oxides.

3. The program is no better than the data used. If there are errors in analytical or thermodynamic data these will be propagated by the program. Many equilibrium constants are only known accurately to an order of magnitude. Some species which exist have never been measured. Other analytical data, such as pE (redox potential), are extremely difficult to obtain.

4. The ionic strength corrections of equilibrium constants used in the program are not accurate above approximately 0.1 M ionic strength and should not be used above 1.0 M, although the program frequently is used for more concentrated solutions with diminished accuracy. At high ionic strength activity coefficients are very difficult to determine and to represent with a simple mathematical formula.

5. The program can violate electroneutrality. Nowhere in the computational scheme of the program is the number of positive charges in a unit volume required to equal the number of negative charges although this is fundamental to the laws of chemistry. Consequently it is possible to have a problem which is poorly specified chemically but which will still undergo computation satisfactorily. When a problem is being set up, the ionic strength guessed or imposed should be approximately correct for the final equilibrium state and the solution should be nearly neutral. Often analytical concentrations do not result in a neutral charge for the solution. If on close inspection (see the example in the following paragraph) the final state shows a great charge imbalance (positive charge not equal to negative charge), the metal or ligand concentrations for the initial input should be modified. The concentration of a non-precitipating, non-complexing ion such as Na^+, NO_3^-, or Cl^- should be changed. It should be a species of high concentration. This is not so great a problem in seawater as it is in dilute solutions.

In order for results to be realistic, the absolute value of the net charge should be at least two orders of magnitude below the ionic strength; in actuality, it should be zero. Consider the results from the sample case shown in Figure 6c and d, pages 62 and 63. Only charged species of concentration greater than 1×10^{-5}M need be considered. Calculation of the net charge of the solution is shown in Figure 1. The net charge is found to be -0.00560 on one liter. The calculated ionic strength is 0.630 mole/liter so in this instance the net charge is less than 1% of the ionic strength and the solution is not far from realistic. Other examples might have a much larger charge relative to the ionic strength.

Figure 1

Calculation of the charge of a solution

Ion	Concentration (mole/l)	Charge	Concentration of charge
Ca^{2+}	2.55×10^{-3}	+2	+0.00510
Mg^{2+}	3.693×10^{-2}	+2	+0.07386
Na^{+}	5.0112×10^{-1}	+1	+0.50112
CO_3^{2-}	4×10^{-5}	-2	-0.00008
Cl^{-}	5.2481×10^{-1}	-1	-0.52481
$CaHCO_3^{+}$	$10^{-3.04} = 9.1 \times 10^{-4}$	+1	+0.00091
$NaCO_3^{-}$	$10^{-4.17} = 7 \times 10^{-5}$	-1	-0.00007
HCO_3^{-}	$10^{-1.21} = 6.163 \times 10^{-2}$	-1	-0.06163
			-0.00560

6. Very small concentrations in the output may be inaccurate; see problems in convergence (Section IV-B, page 31).

7. Atmospheric concentrations of CO_2 and N_2 must be fixed and cannot vary during a computation except to disappear entirely (see Section III-F, page 22).

8. No temperature or pressure variation is allowed for the thermodynamic data in the program which is given for 25°C and one atmosphere.

9. At low concentrations, organic matter which is undetected and uncharacterized may strongly affect equilibria.

III. DATA INPUT AND CONSEQUENT OUTPUT

III-A. SETTING UP A SIMPLE CASE

Figure 2 shows preparation of the input data for metals and ligands for the sample case in Section I-B, page 4. The format and sequence of the cards for program input are shown in Table 4, page 48, and a copy of the input cards for this case is shown in Figure 3.

The program header card (1) shows that this case contains 5 metals (4 plus H^+) and 3 ligands (2 plus OH^-). (Note that HCO_3^- is just CO_3^{2-} combined with H^+). Initially, one case will be run and, to keep it simple, solids will not be imposed or disallowed. This means that if the solution is supersaturated with respect to any solid, that solid will precipitate. Since the pH of the solution has not been measured, the program will compute pH (1 in field 7). Neither redox nor mixed solids will be allowed and ionic strength will be calculated for this case (1 in field 10). All of the normal output will be printed and input concentrations will be in molar units as shown in Figure 2.

Figure 2
Preparation of input data

Solution content	Ionic content	Total ionic content	Reference number from Table 1	-log M
		Metals		
0.5 M NaCl	0.5 M Na^+ 0.5 M Cl^-	Na^+ 0.5 M	5	0.3
		Ca^{2+} 0.1 M	1	1.0
		Mg^{2+} 0.05 M	2	1.3
0.1 M $CaCO_3$	0.1 M Ca^{2-} 0.1 M CO_3^{2-}	Fe^{3+} 0.01 M	6	2.0
		Ligands		
0.05 M $Mg(HCO_3)_2$	0.05 M Mg^{2+} 0.10 M HCO_3^-	CO_3^{2-} 0.20 M*	1	0.70
		Cl^- 0.53 M	3	0.28
0.01 M $FeCl_3$	0.01 M Fe^{3+} 0.03 M Cl^-			

*(CO_3^{2-}) is the sum of all CO_3^{2-} in the system, CO_3^{2-}, HCO_3^- and CO_2. This example assumed no CO_2 is dissolved in the solution water.

Figure 3
Input data cards for sample case

Card Type	Column Numbers 5	10	15	20	25	30
(1)	5 3 1	0 0	0 1	0	0 1	
(2)	1.16E 0					
(3)	1	1.0	1.0			
	2	1.3	1.3			
	5	0.3	0.3			
	6	2.0	2.0			
(4)	1	0.1	0.7			
	3	0.28	0.28			
(5)		8.0				
(6)	0.1					
(7)	0.0					

The second card (2) calls for ionic strength, in this case a guess because the program will be allowed to calculate the ionic strength. Ionic strength is discussed in Section III-C, page 15, and calculation of a guess for it for this case is shown in Figure 4.

The four cards following (2) are the metal cards (3). The metal numbers come from Table 1, page 45, and the calculation of -log M for each ion is shown in Figure 2. An initial guess for the free ion concentration for the first case is needed. Usually this can be taken to be the same as the total concentration. This will cause problems only if almost none of the total concentration (<0.001%) occurs as the free ion. For example, the free concentration of CO_3^{2-} is very small at low pH (0-5). In the case shown the total concentration is taken as the guess, except for CO_3^{2-} where the free concentration is lower (1.0) because it is known that some CO_3^{2-} will be HCO_3^- and not free. More realistic guesses might make the program work more efficiently. For successive cases the free ion concentration guess is the free ion concentration from the preceding case.

The two ligand cards (4) are prepared just as the metal cards (3).

Card (5) requires a guess of pH and, since CO_3^{2-} and HCO_3^- are present, a guess of 8.0 might be made.

Card (6) is required because pH is being calculated. The concept of TOTH is explained in Section III-D, page 17, and calculation of it

Figure 4
Estimation of ionic strength

$$I = (1/2) \sum_{i=1}^{n} M_i Z_i^2$$

where n = number of metals + ligands including H^+ and OH^-.
M_i = concentration of species i
Z_i = charge of species i

For the sample case in Figure 2,

$$I = (1/2)(0.5 \times 1^2 + 0.1 \times 2^2 + 0.05 \times 2^2 + 0.01 \times 3^2 + 0.10 \times 2^2$$
$$(Na^+) \qquad (Ca^{2+}) \qquad (Mg^{2+}) \qquad (Fe^{3+}) \qquad (CO_3^{2-})$$
$$+ 0.10 \times 1^2 + 0.53 \times 1^2 + 10^{-7} \times 1^2 + 10^{-7} \times 1^2)$$
$$(HCO_3^-) \qquad (Cl^-) \qquad (H^+)^* \qquad (OH^-)^*$$
$$= (1/2)(.5 + .4 + .2 + .09 + .4 + .1 + .53)$$
$$= 1.11 \text{ M}$$

*Since H_2O was part of the solution $(H^+) = 10^{-7}$ M for pure water and $(H^+)(OH^-) = 10^{-14}$ then $(OH^-) = 10^{-7}$ M and both are too small to affect ionic strength in this example.

for this example is shown in Figure 5. It is entered as a molar concentration.

Card (7) is required because ligand 1 (CO_3^{2-}) is present. In our case pCO_2 is set to 0.0 which means the water initially in the system is CO_2-free and no CO_2 enters the system from the atmosphere. If CO_2 did enter (or leave) the system it would change both the total amount of CO_3^{2-} and TOTH since CO_2 is considered a complex of H^+ and CO_3^{2-} and contributes two H^+ to TOTH (see Section III-D, page 17).

Cards (8), (9), and (11) are not needed because redox is not considered. Cards (10) and (12) are not required because no solids or mixed solids are considered.

The data as shown in Figure 3 are punched and run as described in Section III-B, page 15. All of the output (7 routines) is reproduced in Figure 6, page 60. These routines are described in detail in Section IV-A, page 26.

Figure 5
Estimation of TOTH[†]

TOTH = sum of the total concentration of all H^+ containing species times the number of H^+ in the species minus the sum of the total concentration of all OH^- containing species times the number of OH^- in the species.

or, stated in symbols,

$$TOTH = \sum_{i=1}^{n} a_i C(H^+)_i - \sum_{j=1}^{m} b_j C(OH^-)_j$$

where the $C(H^+)_i$ and $C(OH^-)_j$ are the total concentration of the species that contain H^+ and OH^- and the a_i and b_j are the number of H^+ and OH^- in those ions.

From the example

$$TOTH = \underset{(HCO_3^-)}{1} \times 0.1 + \underset{(H^+)}{1} \times 10^{-7} - \underset{(OH^-)}{1} \times 10^{-7}$$

$$= 0.1 \text{ M}$$

[†]For further details see Section III-D, page 17.

Figure 6a, page 60, shows the input data for verification. These are the thermodynamic data that the program uses for the specified case and are interpreted in the same way as the thermodynamic data deck card (5) (Section V-A, page 35.) A line of solids and complexes is printed for every possible combination of metal and ligand specified on cards (3) and (4) whether or not they actually form any solids or complexes. 100 log K has been corrected by the program to the guessed ionic strength (Section III-C, page 15).

Figure 6b, page 61, reproduces the input data giving the number of metals and ligands entered, the ionic strength used, the fact that ionic strength will be computed, the initial free ion concentration (-log M) guess for each metal and ligand, and their total concentrations (-log M) for each case. pH is unfixed but guessed to be 8 and TOTH is shown.

Figure 6c, page 62, shows the first case progress. The program required a total of 51 iterations to converge to equilibrium (obtain small enough remainders for each ion). After 36 iterations, the first

solid listed in the thermodynamic data file between Fe^{3+} and OH^- ($Fe(OH)_3$ from data in Figure 6a, page 60) precipitated. After 39 iterations the first solid between Ca^{2+} and CO_3^{2-} precipitated ($CaCO_3$ from Figure 6a, page 60). After 48 iterations, ionic strength corrections were made.

The REDEQL calculated ionic strength is 0.63 M. Notice that this is very different from our estimation of 1.11M. TOTH and the calculated pH, 6.41, are printed. The free concentrations of all metals and ligands are given as M and -log M and their total concentrations (which are the same as the input) are also shown as M and -log M. The remainders are used by the program in determining how many iterations are necessary.

The amounts of two solids which precipitate are given and for $CaCO_3$ this is 0.0964 moles/l while all of the Fe^{3+} precipitated as $Fe(OH)_3$.

Figure 6d, page 63, shows the concentration of complexes. For instance, the 1 1 0 complex of Ca^{2+} and CO_3^{2-} (1 Ca^{2+}, 1 CO_3^{2-}, 0 H^+) has a concentration of $10^{-5.3}$ moles/l while the concentration of the 1 1 1 complex of Ca^{2+} and CO_3^{2-} (1 Ca^{2+}, 1 CO_3^{2-}, 1 H^+) is $10^{-3.03}$ or ($CaHCO_3^+$) = $10^{-3.03}$ mole/l. Generally, complexes with -log M greater than 8 are of no interest but this depends on the total concentration of the species. This output tells us that (HCO_3^-) = $10^{-1.21}$ M and (H_2CO_3) = $10^{-1.57}$ M. In the output for speciation of ions (Figure 6e, page 63) the free concentration of each ion is given and the concentration of each ion that is paired with another is listed. For example, there are $10^{-1.05}$ moles/liter of H^+ and CO_3^{2-} complexes. They are (from the concentration of complexes output) (HCO_3^-) = $10^{-1.21}$ M and ($H_2CO_3^+$) = $10^{-1.57}$ and their total is $10^{-1.05}$ M. This output is a combination of data from the concentration of complexes output (Figure 6d, page 63) in a more convenient form. A row of stars signifies a number greater than 100 which is a very small concentration.

The primary distribution of metals and ligands (Figure 6f, page 64) shows all species which compose more than 0.5% of the total concentration of a metal or ligand. For instance 48.3% of the CO_3^{2-} is precipitated as $CaCO_3$, 44.6% is complexed with H^+ as HCO_3^- and H_2CO_3, and 6.5% is complexed with Mg^{2+} as $MgHCO_3^+$ and $MgCO_3^0$. The stoichiometry of the complexes has been taken from the concentration of complexes output (Figure 6d, page 63).

Figure 6g, page 64, is the thermodynamic data used after ionic strength corrections have been completed. Observe, that, for $CaCO_3(s)$, $(Ca^{2+})(CO_3^{2-}) = 10^{-7.0}$ at ionic strength of 0.63, while at ionic strength of 1.11, this solubility product (the inverse of the formation constant) was $10^{-7.1}$. From the thermodynamic data deck the solubility product at zero ionic strength is found to be $10^{-8.3}$. Further examples of input and output will be given in the following sections.

III-B. RUNNING REDEQL.EPA ON THE EPA COMPUTER SYSTEM

The input cards described in Section III-A, page 10, and Table 4, page 48, are placed within a set of control cards in order to run the program on COMNET at the Washington Computer Center (WCC), Washington, D.C. The program is run from a load module and also requires the thermodynamic deck MREHT or another data deck as described in Section V-B, page 40.

The following control cards are required:

```
//(Job Card.............),TIME=2,
// REGION=250K,MSGLEVEL=(0,0)
//  EXEC  PGM=SARRUN
//STEPLIB DD DSN=CN.EPABDJ.CPR1.HUNS,DISP=SHR,UNIT=3330-1
//FT05F001 DD  DDNAME=SYSIN
//FT06F001 DD  SYSOUT=A
//FT10F001     DD DSN=CN.EPABDJ.CPR1.MREHT,
//  DISP=SHR,UNIT=3330-1,VOL=SER=USER60
//GO.SYSIN  DD  *
     (Insert input cards here)
/*
```

III-C. IONIC STRENGTH AND CORRECTION OF THE THERMODYNAMIC DATA FOR IONIC STRENGTH.

Ionic strength (I) is defined by

$$I = (1/2) \sum_{i=1}^{n} M_i Z_i^2$$

where M_i is the molarity (molar concentration) of ion i and Z_i is the charge on that ion. The ionic strength is unaffected by uncharged species in solution but depends on all ions including complex ions in solution. Ionic strength for the program can be estimated from the input concentrations of ions, but complexation and precipitation among reactants will reduce ionic strength. Normally one would want the program to calculate ionic strength, unless working in a solution of very constant ionic strength (such as seawater), because ionic strength is not easy to estimate accurately.

Ionic strength is required by the program to adjust thermodynamic data to the solution considered. The thermodynamic data on file are for infinite dilution. For each computation the program makes, the data are corrected with either an imposed ionic strength or an ionic strength computed by the program from the equilibrium concentrations of ions and complexes present as described above. The extension of the program to seawater and other solutions of high ionic strength is limited by the accuracy of the thermodynamic data at 25°C corrected with activity coefficients γ calculated from the Davies (5) equation:

$$-\log \gamma(|Z|) = 0.509\ Z^2 \left(\frac{\sqrt{I}}{\sqrt{I}+1} - 0.2\ I\right) \qquad (2)$$

where $|Z|$ is the absolute value of the charge and I is the ionic strength. This equation is used to find the log of the activity coefficients for all ions with charge Z except H^+ whose value is taken as 1/2 log $\gamma(1)$.

K_I (K corrected to ionic strength I), is related to K at infinite dilution through the activity coefficients. For example, for

$$Fe^{3+} + 2\ Cl^- = FeCl_2^+ , \qquad (3)$$

$$K_I = \frac{(FeCl_2^+)}{(Fe^{3+})(Cl^-)^2} = \frac{K\ \gamma(3)\gamma(1)^2}{\gamma(1)} = K\ \gamma(3)\gamma(1). \qquad (4)$$

K is listed in the thermodynamic deck, the $\gamma(|Z|)$ are calculated from the Davies equation, and then K_I is calculated according to equation (4).

It has been shown in Section III-A, page 10, how ionic strength corrections affect the thermodynamic data. Figure 7, page 65, shows the same deck as Figure 3, page 11, but this time without ionic strength calculations. The thermodynamic input for verification (not shown) is exactly as that first listed in Figure 6a, page 60, but the case progress is different and of course the free ion concentrations are different. Ionic strength is not listed after each case because it is fixed in the input data. Notice that the program converged after 48 iterations because it did not make ionic strength corrections (compare with Figure 6c, page 62).

III-D. $TOTH = \Sigma H^+ - \Sigma OH^-$

TOTH is a way of counting one more species (like a metal or a ligand) in all of its combined and uncombined forms. The species is H^+ and like any other species it can be free or combined. pH is a measure of the amount of free H^+, $pH = -\log (H^+)$, and if pH is fixed (given) the program can use all the thermodynamic constants to determine how much combined H^+ exists, and the sum of free and combined H^+ is TOTH. If pH isn't fixed, the program does the opposite calculation, using the value for total H^+ supplied as TOTH and the thermodynamic constants to calculate free H^+ (pH).

Unlike other species in the program, TOTH may have a negative concentration because from the total H^+ one must subtract total OH^- since every OH^- has the potential of annihilating one H^+ in the reaction:

$$H^+ + OH^- = H_2O \qquad K_{H_2O} = (H^+)(OH^-) = 10^{-14} \qquad (5)$$

At pH greater than 7, there is more free OH^- than H^+; TOTH may or may not be negative, however, because TOTH includes combined H^+.

TOTH is readily calculated if one knows the concentrations of the compounds being put into solution. One simply adds the concentrations of H^+ and subtracts the concentrations of OH^- (written as $-H^+$) in solution. Remember that some species, namely nonmetal oxides, form acids (H^+ donors) in water. For example,

$$CO_2 + H_2O = H_2CO_3 \qquad (6)$$

so each mole of CO_2 in solution will provide two moles of H^+. (Remember,

too, that even if CO_2 is not put in solution, it may diffuse in from the atmosphere, especially if the solution is of high pH.) Other species, metal oxides in particular, react with water to give bases (OH^- donors). For example,

$$Al_2O_3 + 3H_2O = 2\ Al(OH)_3 \qquad (7)$$

so that each mole of Al_2O_3 is providing six moles of OH^-.

Notice that, for both metal and nonmetal oxides, a whole water molecule is added, not split. Na_2CO_3 gives a basic solution in water because of the reaction

$$CO_3^{2-} + H_2O = HCO_3^- + OH^-. \qquad (8)$$

The solution is basic because there is more free OH^- than H^+, but TOTH is zero because Na_2CO_3 contains neither H^+ nor OH^- and even after reacting with water there is an equal amount of HCO_3^-, which adds to TOTH because of the H^+ in it, as the amount of OH^- which subtracts from TOTH.

Some examples (Figure 8) will illustrate the TOTH concept for solutions made from stock chemicals. Consider the classification of compounds below as acids (H^+ donors) and bases (OH^- donors).

Acids (H^+ donors)	Bases (OH^- donors)
CO_2 or H_2CO_3	NaOH, Na_2O, KOH
$NaHCO_3$, H_3PO_4, NaH_2PO_4, Na_2HPO_4	CaO, $Ca(OH)_2$, $Mg(OH)_2$
HCl, H_2SO_4, $NaHSO_4$	$Fe(OH)_3$, Fe_2O_3
NH_4Cl, CH_3COOH, RCOOH	$Al(OH)_3$, Al_2O_3
H_2SiO_3, SiO_2	ZnO, PbO_2, CuO
H_2S	$M(OH)_n$**
H_mL*	

*L = ligand
**M = metal

Figure 8
TOTH sample calculations

1. A system made up of 2 mole $NaHCO_3$, 0.5 mole Na_2CO_3, 0.2 mole NH_4Cl, 0.8 mole NaH_2PO_4, 1.0 mole $Ca(OH)_2$, and 0.5 mole $Fe(OH)_3$ in one liter of solution.

chemical	concentration (M)	moles H^+/mole	moles H^+/liter
$NaHCO_3$	2.0	1	2.0
Na_2CO_3	0.5	0	0
NH_4Cl ($NH_3 \cdot HCl$)	0.2	1	0.2
NaH_2PO_4	0.8	2	1.6
$Ca(OH)_2$	1.0	-2	-2.0
$Fe(OH)_3$	0.5	-3	-1.5
		TOTH =	0.3

2. A system with 10^{-1}M CO_2, 10^{-1}M $NaHCO_3$, 10^{-1}M CaO, and 10^{-1}M $CaCO_3$.

CO_2 (H_2CO_3)	1×10^{-1}	2	2×10^{-1}
$NaHCO_3$	1×10^{-1}	1	1×10^{-1}
CaO ($Ca(OH)_2$)	1×10^{-1}	-2	-2×10^{-1}
$CaCO_3$	1×10^{-1}	0	0
		TOTH =	1×10^{-1}

3. A system with 1×10^{-2}M $Al(OH)_3$ and 1×10^{-2}M SO_3

$Al(OH)_3$	1×10^{-2}	-3	-3×10^{-2}
SO_3 (H_2SO_4)	1×10^{-2}	2	2×10^{-2}
		TOTH =	-1×10^{-2}

An estimate of TOTH is difficult to make for solutions for which one has only analytical data. A measure of CO_3^{2-}, for example, generally includes total CO_3^{2-} and HCO_3^-, but for TOTH only HCO_3^- and H_2CO_3 are counted and H_2CO_3 counts twice because it can donate 2 H^+. One must calculate from an estimated pH how much of the CO_3^{2-} exists in complexes, as H_2CO_3, as free HCO_3^-, or in HCO_3^- complexes. The thermodynamic data for acid dissociation complexes can be used from the thermodynamic data deck, so that knowing K and K_c for such things as:

$$K = \frac{(HCO_3^-)}{(H^+)(CO_3^{2-})} \quad \text{and} \quad K_c = \frac{(CaHCO_3^+)}{(Ca^{2+})(HCO_3^-)} \qquad (9)$$

where all concentrations are free, one can estimate total HCO_3^- concentration with the restriction that

$$(CO_3^{2-})_{analytical} = (CO_3^{2-})_{total} + (HCO_3^-)_{total} \qquad (10)$$

(excluding H_2CO_3 in this case). HCO_3^-, if present, will probably be the most important species in estimating TOTH, but any other incompletely dissociated acids or bases will also contain H^+ or OH^-. Possibilities for a particular system will be found by scanning the thermodynamic data for metal-ligand-H^+ (OH^-) complexes, metal complexes with ligand 99, or metal 50 (H^+)-ligand complexes.

At pH less than 7 the amount of free OH^- is negligible and the free H^+ concentration is determined by

$$pH = -\log (H^+).$$

Above pH 7, H^+ is negligible and free OH^- is given by

$$-\log(OH^-) = 14 - pH$$

It is not a good idea to estimate TOTH from a guessed pH because the program will regenerate the guessed pH unless the calculations used to get TOTH from the guessed pH were inaccurate.

A sample calculation with TOTH given and pH calculated has been shown in Figures 3, page 11, and 6, page 60. Figure 9, page 66, shows three cases with fixed pH. Notice the TOTH card (6) is not used. Fixing pH negates the assumption that the system initially had 0.1 mole of CO_3^{2-} and 0.1 mole of HCO_3^- although in the first case the total CO_3^{2-} concentration is specified in solution as 0.2 M. In the second and third case this is no longer true. Removal of the constraint that $pCO_2 = 0$ allows the solution to equilibrate with atmospheric CO_2 (see also Section III-F, page 22). Some of the 0.2 moles/liter CO_3^{2-} may then be in the atmosphere as CO_2 and not in the solution at all. This will <u>not</u> change pCO_2. In the second case 51.7% of the CO_3^{2-} is CO_2 and essentially all of it is CO_2 in the third case. Note that CO_2 is denoted a <u>solid</u> formed from two H^+ and CO_3^{2-}. It is treated as a solid by the computational scheme and appears in the thermodynamic data for solids under metal 50, ligand 1. pCO_2 has been included in the value of K for formation of H_2CO_3. Notice also that TOTH in the first case is smaller than the fixed TOTH used previously while TOTH for the second and third cases is larger. The increase is due to the increase in CO_2 in the second and third cases.

The output routine which prints the input data records pCO_2 for the third case as 0.0 while it is intended to be 3.5. However, as with

the input cards, this 0.0 will be replaced by the preceding case when the program runs, and, in checking the progress for case 3 output, page 69, this is found to be true.

III-E. SOLIDS: IMPOSED AND NOT ALLOWED TO PRECIPITATE

All or any combination of solids (up to 13) can be allowed to supersaturate the solution. To do this, the program removes the solid from the data file. This option might be used, for instance, when seawater is known to be supersaturated with respect to $CaCO_3$.

As an example in which no solids are allowed, consider the output from the data deck shown in Figure 10a, page 71. The thermodynamic data show no solids and the free concentrations in the case progress are different from those in Figure 6c, page 62, where solids were allowed to precipitate. The distribution of species is also modified. This solution is now supersaturated with respect to $CaCO_3$ and $Fe(OH)_3$ but there is no way to determine this from the output in Figure 10, page 71. It must be compared to the output in Figure 6e, page 63.

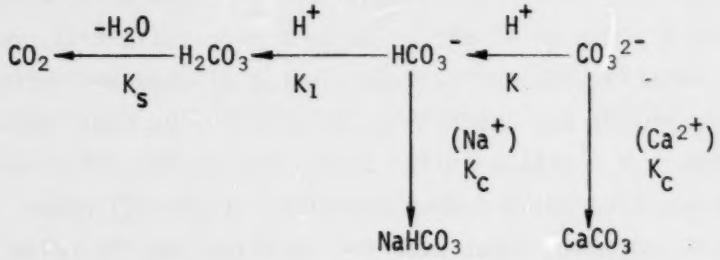
Solids can also be assumed to be present (imposed), although they will dissolve if the solution is not saturated with respect to them. One might use this option if the solution in question were known to be in contact with a solid or if one is quite sure a solid will precipitate. In Figure 11, page 73, one solid, $CaCO_3$ is not allowed and $MgCO_3$ is imposed. These solids are identified on card (10) by their metal, ligand and solid number. A positive solid number imposes the solid for the <u>first</u> case; a negative solid number disallows it for <u>all</u> cases. Notice that in the thermodynamic input data for verification the value for log K of $CaCO_3$ has been removed, so $CaCO_3$ will not precipitate and that the imposed solid is listed at the end of the input data output routine. Be sure, by checking the case progress, that the imposed solid does not dissolve because, if it does, the assumption of contact of the solid with the solution is wrong. The program will give the same results whether or not a solid is imposed, so long as a number which is too large or too small is not generated in the computational process. If a solid phase is to remain in contact with the solution, be sure to allow an excess of the ions it contains.

In general, for small systems it is easier not to impose solids. For larger systems the program will converge more rapidly if correct solids are imposed, but convergence is even harder to obtain if incorrect solids are imposed.

III-F. GAS PHASE, pCO_2

If the solution is in equilibirum with a gas phase (for example, air), partial pressures for CO_2 and/or N_2 are required for each case. Typical atmospheric values are -log CO_2 = 3.5 and -log N_2 = 0.1. $CO_2(g)$ and $N_2(g)$ are treated as solids in the computer system since they are a phase other than the aqueous phase. CO_2 will be listed as a solid containing 2 H^+ and 1 CO_3^{2-}. N_2 is listed as a solid containing 2 NO_3^- and 12 H^+ when redox is allowed and NO_3^- is present. These gases will be listed under these stoichiometries in the thermodynamic input data for verification, in case progress, and in the primary distribution of species.

When an atmospheric value of CO_2 is given for an equilibrium system, it sets, through all possible equilibria, the amount of CO_2 in every other possible form because of the reactions diagrammed below.



Many more complexes are formed than the two shown above. Details of carbonate chemistry may be found in texts such as that of Stumm and Morgan (4). The amount of each species will depend upon pCO_2, the constants, and free concentrations of H^+, Na^+, and Ca^{2+} for the example given. When pCO_2 is not given, the total CO_3^{2-} for the case is divided according to the thermodynamic constants among all possible forms. When pCO_2 is given, the total CO_3^{2-} given must be greater than the sum of all CO_3^{2-} species in equilibrium with that pCO_2. This means excess CO_2 will

just escape from the system. The imposed atmospheric pCO_2 is unaffected by "precipitation of CO_2" because the atmosphere is assumed large enough and sufficiently mixed that CO_2 added to the atmosphere from the solution does not change the pCO_2.

However, if H_2CO_3 dissolves when the program begins iterations, it means that no CO_2 remains in the atmosphere because the system was not given sufficient total CO_3^{2-} to be in equilibrium with the atmospheric CO_2. The solution is undersaturated and "CO_2 dissolves" leaving no CO_2 in the atmosphere but not increasing total CO_3^{2-}. This obviously is not what one would expect to happen in a system in equilibrium with CO_2 in the atmosphere. To avoid this situation total CO_3^{2-}should be given as about 0.1 M or even larger at high pH.

III-G. REDOX COMPUTATIONS

When redox reactions are considered, be sure that all metals and ligands (as listed in Table 1, page 45) in the reactions specified on card (11) have been included in the metal and ligand cards, (3) and (4), and determine a value for pE, -log (electron activity), in the system. Typical values of pE in aqueous solutions range from -4 (reducing) to 12 (oxidizing). For elaboration of the concept of pE see Chapter 7 of the text by Stumm and Morgan (4).

Judicious selection of redox equations is essential for proper functioning of the program. If the pH and pE of the computation are such that the concentration of a redox species is less than 10^{-10}M or a ratio of concentration of species linked by redox is less than 10^{-5} or greater than 10^5, species involved should be put in the program as the dominant form and redox should not be considered. For example, put all iron in as Fe^{2+} below pE = 6. Above pE = 6 put the total concentration of iron in as Fe^{2+}, Fe^{3+}, or some combination of the two and include redox reaction 1. NO_3^- may be reduced to NH_3 or NH_3 may be oxidized to NO_3^-. This can depend on pH as well as pE. For example, at pE = 6, nitrogen should be considered as NO_3^- above pH 8, as NH_3 below pH 4, and as a mixture of the two with the redox reaction allowed between pH 4 and 8.

It is recommended in using redox reactions to introduce only one reaction at a time and not to vary pE and pH greatly between cases. In this way it is easier to trace which reaction is causing a problem such as non-convergence (see Section IV-B, page 31) should it occur.

Caution must be exercised in using the redox reactions because the kinetics of some are very slow, particularly the nitrogen reactions and those involving oxidation of solids. If one is interested in short-term effects, some redox reactions might not be included because of their slow rates of reaction or because biological activity maintains the concentrations which are not at equilibrium chemically. As an example, consider that NH_3 and NO_3^- often occur simultaneously in aquatic systems where their coexistence is not predicted by the program. Whether this is caused by slow interchange (redox) or constant supply of one of them doesn't really matter. The user would want to leave both in the system and not use a redox equation.

Use of a redox reaction is illustrated in Figure 12, page 76. This computation is the same as Figures 3, page 11, and 6, page 60, but now also includes a redox reaction so a pE card (8) and a redox card (11) are needed. A pN_2 card is not needed as NO_3^- (ligand 57) is not included. Four cases from pE 12 to pE -4 are considered. The redox reaction considered is 1 and, since Fe^{2+} is not part of the input, a metal card (3) must be added for it. The concentration of Fe^{2+} is made very small so as not to change the total iron concentration and since the first case is oxidizing, the free ion concentration of Fe^{2+} will probably be low. The first thermodynamic input data for verification output is shown along with the four case progresses.

III-H. MIXED SOLIDS

Mixed solids and clays are treated just as solids in Section III-E, page 21. Once mixed solids are specified by a 1 in field 9 of the program header card, all mixed solids are allowed to precipitate when the solution is saturated with respect to them unless a mixed solid is imposed (postive) or not allowed (negative) on the mixed solid card (12). An example in which dolomite is allowed to precipitate but no

other mixed solids may precipitate because they are not allowed and also because some of their components are missing in the solution is shown in Figure 13, page 82. The thermodynamic input data for verification, the case progress, and the primary distribution of species outputs are shown.

III-I. MILLIGRAM/LITER INPUT AND OUTPUT

An option for mg/l input data is available by placing a 1 in field 17 of the program header card (1). This option has been introduced because field data is more often available in this form than in moles/l. Input data in this form produce the normal output routines except that the input data reproduced will be in mg/l and the case progress gives concentrations of all species in mg/l. The concentration of complexes and speciation of metals output routines will have concentrations in moles/l. Examples of input cards, input data output, and case progress are shown in Figure 14, page 84.

IV. PROGRAM OUTPUT

This section of the guide contains descriptions of both standard output and undesired problem output.

IV-A. NORMAL OUTPUT

The output for the program if only zeros are placed in fields 11-16 of the program header card (1) appears in six printed formats. A seventh showing interaction capacity and intensity is available by placing 1, 2, or 3 in field 11 of the program header card. These seven outputs are described in order of appearance below. See Table 5, page 54, for references to examples of each of these outputs.

1. Thermodynamic input for verification

The first page of output is labeled input data for verification. It is the input thermodynamic data corrected to the ionic strength given on input card (2) (see Section III-C, page 15). This data format is identical to that described in the thermodynamic data cards (5) in Table 6, page 55, except more widely spaced and the numbers given are 100 log K rather than 10 log K. A line is shown for every possible metal-ligand pair from those specified in the program input cards (3) and (4). In any line the first number is the metal reference number, the second the ligand reference number, and these are followed by nine groupings of numbers, three for solids and six for complexes. Within each grouping the first number is 100 log K and this is followed by the stoichiometric coefficients of the metal, ligand, and H^+ (OH^- if negative) respectively. The log K values are not the same as the thermodynamic data because they have been corrected for ionic strength. If a solid is not allowed, it will not be listed in these data.

If mixed solids are considered, mixed solids data for those solids whose components are included in the metal and ligand input cards will be listed below the data for solids and complexes, unless the mixed solid is not allowed. The mixed solid number from Table 3, page 47, is

given first. The number preceding the M (or L) is the stoichiometric coefficient of that metal (or ligand) whose reference number from Table 1, page 45, is within the parentheses. The number of hydrogens in the solid is shown and is followed by 10 log K corrected for ionic strength.

Redox data are recorded but are identified neither by reaction number nor name so they are hard to identify. The names of the reactions are listed in the next output routine of the input data. In the thermodynamic input data for verification routine, the type of redox reaction is printed (KRED), then the two species (MREDOX and LREDOX) which are involved in the reaction (metal-metal, ligand-ligand, or metal-ligand), identified by their position (first, second, third, etc.) among the input metals and ligands for the particular run, are printed. The number of electrons produced (NELEC) and H^+ consumed (NHRED) are also shown, along with 100 log K (REDCST) corrected for ionic strength.

This output is repeated after each case when ionic strength corrections are being made by the program. The output after each case (but not initially) may be suppressed by placing a 1 in field 16 of the program header card. Only in the printout of this output after each case will $H_2CO_3(s)$ (CO_2) or $H_{12}(NO_3)_2(s)$ (N_2) appear.

2. Input data for the program calculation

The second page of output describes the input data from the cards read into the computer. The first line tells how many metals and ligands were used and how many solid and complex equilibria were used. The second line is the ionic strength as shown on input card (2). If ionic strength is to be calculated and corrections performed on the constants, this is stated. The number of cases considered is listed. After this, the metal and ligand data are blocked out exactly as on the input cards but with the metals and ligands labeled. After the blocked out data, a line tells whether pH is fixed or not, the pH values for fixed pH or the pH guess for the first case followed by all values of TOTH if pH is to be computed.

If any CO_2 pressures are on the pCO_2 input card (7), pCO_2 values for all cases will be listed. A zero following a non-zero value for pCO_2 will be treated as the non-zero value.

The redox potential, pE, will be listed in each case if redox is considered.

All solids which are imposed are listed by metal, ligand, and place (first, second, or third) in the thermodynamic data list, and mixed solids imposed are listed by number (from Table 3) and components.

Redox reactions considered are listed by the name given them in columns 46-53 of the redox reaction cards (7) from the thermodynamic data deck.

3. Case progress for each case

The output routine for the first case progress will follow the two routines above. After it prints all the following routines, the program will print case progress for the second case, the following routines, case progress for the third case, etc.

The case progress routine gives a brief outline of what is happening during successive program iterations for the case in question. The final free concentrations (not complexed or in solids) of all species are given as well as the "concentration" of solids and gases. i.e., how much of the solid or gas precipitated from one liter of the initial solution. Each time the program determines that the solution is supersaturated with respect to a solid which could precipitate or undersaturated with respect to a solid with which it is in contact, the solid which precipitates or dissolves is printed under the number of iterations done up to that point. The number of iterations with no other notation is also printed every time the ionic strength is recalculated. The last number of iterations is the number required to obtain convergence. The smaller the number of iterations, the more efficiently the program ran because of a simple case or good guesses of free concentrations, pH, ionic strength, imposed solids, etc.

The ionic strength is printed if calculated. TOTH and pH are printed. pE is printed if redox is included. The free concentrations

and total concentrations are printed in mole/l or mg/l. The total concentrations should agree with the input data unless two species are linked by redox (see Section III-G, page 23) in which case the sum of their total concentrations may appear under one or the other. A remainder is the difference between the total concentration of a metal or ligand and the sum of concentrations calculated for that species in all of its forms. It must be less than 0.01% of the total concentration for convergence.

The total amounts of solids and mixed solids in contact with one liter of solution are given. The solids are identified by their metal, ligand, and solid number 1, 2, or 3 representing whether it is the first, second, or third solid listed in the thermodynamic data.

This output can be suppressed by a 1 in field 12 of the program header card.

4. Concentration of complexes

The concentration of complexes output, unless suppressed by a 1 in field 13 of the program header card, follows case progress for each case. For each metal and ligand which form a complex the metal, the ligand, -log M for the complex, and the stoichiometric coefficients of the metal, ligand, and H^+ (OH^- if negative) are given.

5. Speciation of the metals and ligands

Speciation of the metals and ligands is given after the concentration of complexes output unless suppressed by a 1 in field 14 of the program header card. The output is blocked out in a matrix of metals and ligands. The free concentration of each metal and ligand is given as -log M and the sum of all concentrations of all complexes of a given metal and a given ligand is given as -log M. The free concentrations are the same as those shown in the case progress output. The individual complexes which sum to the total complex concentration can be found in the preceding complex concentration output.

6. Primary distribution of metals and ligands

The output for the primary distribution of metals and ligands, unless suppressed by a 1 in field 15 of the program header card, shows the form (free, bound or complexed with some other species, or in solid form with another species) and percentage of any fraction of a metal or ligand which comprises more than 0.5% of the total concentration of that metal or ligand.

7. Interaction capacities and/or intensities

Interaction capacity and intensity are measures of how strongly the concentration of one species is affected by a change in concentration of another species. In the output and for the following, the X component is listed vertically and the Y component is listed horizontally and they are both all the metals and ligands used in the case shown.

Capacity, $\delta'_{X,Y}$, is defined by

$$\delta'_{X,Y} = \frac{\partial p(X)}{\partial TOTY} \tag{14}$$

Where p(X) is -log of the free concentration of the X component and TOTY is the total concentration of the Y component.

Intensity, $\delta_{X,Y}$ is defined by

$$\delta_{X,Y} = \frac{\partial p(X)}{\partial p(TOTY)} \tag{15}$$

where p(X) is as above and p(TOTY) is -log of the total concentration of the Y component.

$\delta'_{X,H}$ is always printed instead of $\delta_{X,H}$ because the latter cannot be defined in general since TOTH can be zero or negative. For a complete explanation of the concept of interaction capacities and intensities see Morel et al. (3). This output appears only when 1 (capacities), 2 (intensities), or 3 (both) is entered in column 33 of the program header card.

A portion of an interaction capacity output is shown in Figure 15, page 86. In the first column -195 indicates that a small change in the total Ca^{2+} concentration sharply decreases the free Mg^{2+} concentration while -0.0003 indicates the free K^{+} concentration is relatively unaffected by changes in the total Ca^{2+} concentration.

IV-B. ERROR MESSAGE OUTPUT

Both program- and system-generated error messages are considered to be problem output. Actually any output that gives an undesired result is problem output. Four program-generated error messages may occur:

1. Be careful - no convergence

This message is generated in the case progress output when 200 iterations have been made. An example is shown in Figure 16, page 87. Two possible reasons why convergence might not be obtained are:

(a) If a large solid set is generated or for very large computations, the system may be converging although more iterations are required. In this case the remainders will be smaller than the total concentrations shown on the case progress. To correct, run again using the free concentrations shown on the case progress and imposing the solids listed there and no others.

(b) If the system has diverged, the values of the remainders will be larger than the respective total concentrations for some species. Thus by comparison of the remainders and total concentrations the problem areas of the computation may be identified. Also, ridiculous concentrations may be apparent such as that shown for free Ca^{2+} and $CaCO_3(s)$ in Figure 16, page 87. This particular output was obtained when pE was varied from case to case. A slight change in total or guessed concentrations might remove the problem. Further information can be obtained from the listing of complex concentrations. By hand calculation of a small subsystem in which the problem is suspected to originate, better

guesses can be made as to free concentration and imposed solids and then the program run again with these guesses. As mentioned before, be especially careful when considering redox reactions and varying pE and pH.

Two particularly bad cases for obtaining convergence are:

(1) If both a metal M and a ligand L are nearly all bound in a strong complex C, i.e., $K = (C)/(M)(L)$ is very large and the total concentration of the metal is approximately the same as the total concentration of the ligand, e.g., $K = 10^{20}$, $(C) \simeq 10^{-2}$, total concentration of metal = total concentration of ligand = 10^{-2}, then $(M) = (L) = 10^{-11}$ but the equation is also satisfied within the precision of the program when $(M) = 10^{-13}$ and $(L) = 10^{-9}$.

(2) If a solid with small K is computed from a large equation, e.g., the total concentration of $Ca^{2+} = 10^{-1}$ and the total concentration of $PO_4^{3-} = 10^{-8}$, and $Ca_5(PO_4)_3OH$ is present, very small changes in the concentration of either Ca^{2+} or PO_4^{3-} can give very different solubility results because of the large stoichiometric coefficients.

2. Error return from GAUSSL - Diagonal term reduced to zero

This message is generated if one of the terms on the diagonal of a computational matrix becomes zero. This is highly unlikely for a properly specified system. To correct this situation carefully check the conditions of the problem specified. The input cards for metals and ligands have probably been prepared incorrectly (see Section III-A, page 10).

3. Gibbs phase rule violated in subsystem

This message is generated when a solid set is imposed which is inconsistent with Gibbs phase rule. Gibbs phase rule is a limitation on the number of solid, liquid, and gas phases that can coexist. This is a physical limitation not a program limitation and is similar to the reason why ice, water, and water vapor do not coexist in equilibrium at

25°C and one atmosphere pressure. This program allows at most one gas and one liquid phase, but each solid is a different solid phase. When too many solids are imposed initially, Gibbs phase rule will be violated. To correct this situation, restart the computation with a set of imposed solids consistent with the phase rule (fewer solids).

The fact that the preceding case is used as a guess for the next case may also cause phase rule problems when the preceding case precipitated solids because those solids are imposed on the next case and, if pE, pH or some other parameter is radically different between the cases, those solids probably should not be imposed. A much less likely cause for violation of Gibbs phase rule is that the program did not generate the set of solids for the case correctly. A better guess of the solids to impose should be made in this instance.

4. Repeated precipitation-dissolution

Under some circumstances the program will precipitate a solid phase and then dissolve it, repeatedly. It is likely in this case that another solid (possibly in the same row of thermodynamic data) should be precipitated instead. To correct, restart the computation with the suspected correct solid imposed.

System generated program errors which are likely to occur are shown below.

5. IHN208 Underflow - this message has been suppressed but the error is generated as the result of computation of a number too small in magnitude for the computing system, e.g., a species with a concentration of 10^{-100} M. This error can be ignored, but the number of times it occurred is printed at the end of the program output.

6. IHN217 End of data on unit 5

7. IHN205 Illegal decimal character - These messages (6 and 7) are generated by any of the input routines as the result of incorrect input data cards. The input cards should be carefully checked against the

sequence, formats, and total number of cards specified in Table 4, page 48, and Section III, page 10.

8. IHN207 Overflow - This message may be generated as the result of computations of very large numbers (10^{+72}). Such a condition normally will not allow the program to converge, and the computation will be terminated by default after ten of these errors occur. This situation will usually be caused by the computations of redox systems over a wide range of pE. Care should be taken in performing such computations so that redox species at extremely small concentrations are not included in the chemical system (see Section III-G, page 23).

9. IHN209 Divide check - This message is generated when division by zero occurs. It may be caused by a total concentration set to zero unintentionally. Particularly in the first case of mg/liter total concentration input, be sure to make the total concentration $\geq 10^{-14}$ mg/l.

10. IHN253 Argument of a log is equal to or less than zero - This error usually occurs when other errors described above have been made.

V. THERMODYNAMIC DATA

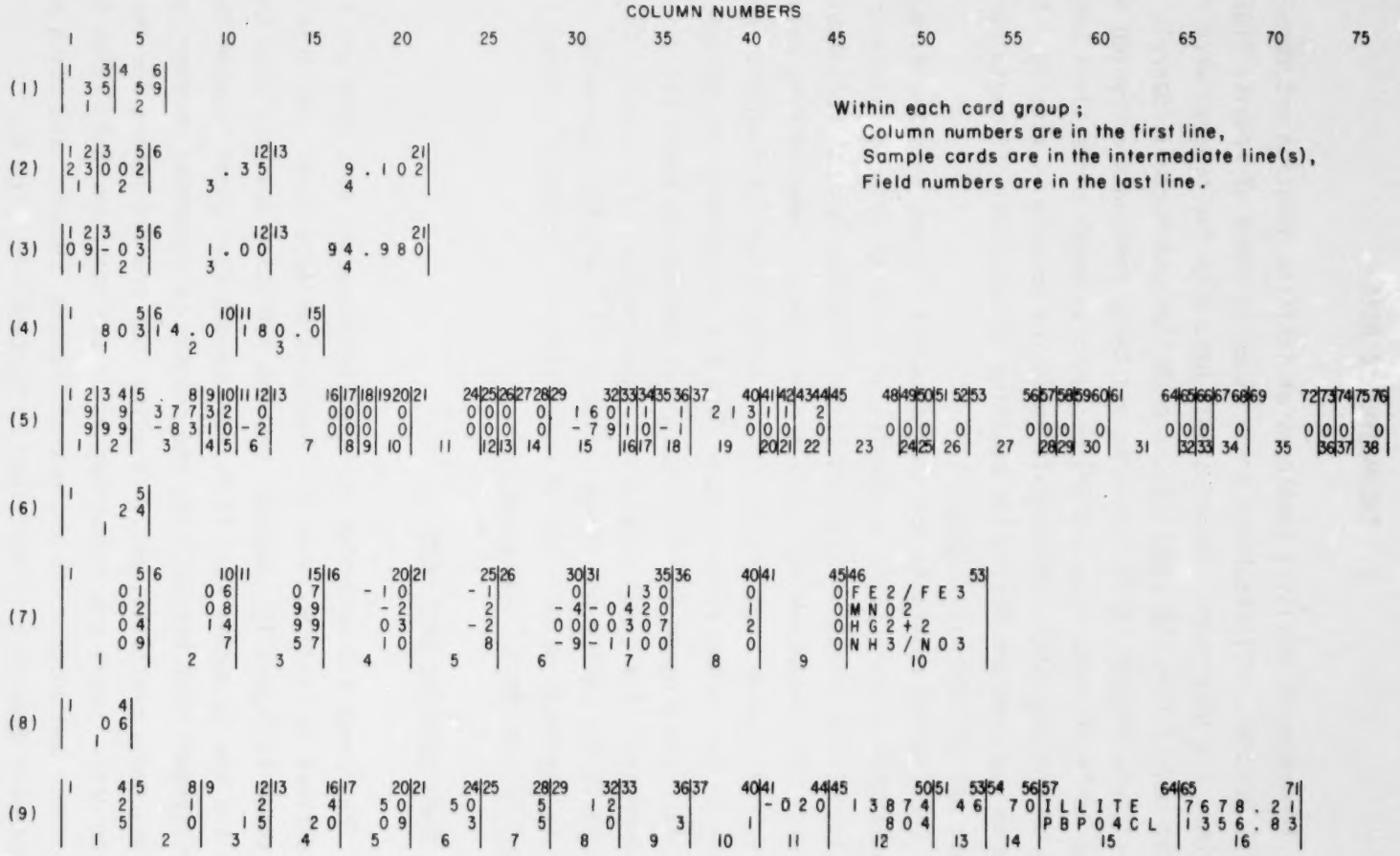
Formation (stability) constants at infinite dilution are required by the program. All reactions are written in terms of metals, ligands, protons, and electrons. The constants used with the program were selected mainly from the compilations of Sillen and Martell, Garrels and Christ, and Ringbom (6-9). One can use these constants corrected to a given ionic strength (e.g., 0.5M) or ionic strength corrections can be made on the constants continuously while the program is running. The program now uses the Davies (5) equation to make ionic strength corrections; see Section III-C, page 15.

Equilibrium constants are stored as log K where K is the formation constant for a given solid or complex at infinite dilution. For solids, the log of the formation constant is the negative log of the solubility product. All formation reactions are written in terms of free metal ions, free ligands, and protons (H^+). Calculations of formation constants to use in the thermodynamic data are illustrated in Section V-C, page 41. The program design allows for a maximum of three solids and six complexes of a given metal-ligand combination. For example $Ca_5(PO_4)OH$, $Ca_4H(PO_4)_3$ and $CaHPO_4$ are three solids of Ca^{2+} and PO_4^{3-} currently listed and six complexes of Ni^{2+} and NH_3 are $Ni(NH_3)^{2+}$, $Ni(NH_3)_2^{2+}$, $Ni(NH_3)_3^{2+}$, $Ni(NH)_3)_4^{2+}$, $Ni(NH_3)_5^{2+}$ and $Ni(NH_3)_6^{2+}$.

V-A. THERMODYNAMIC DATA DECK

The format and variables for the thermodynamic data deck are listed and defined in Table 6, page 55. Examples of data lines from this deck are shown in Figure 17, page 36, and the following text explains the deck and how to modify it. It is recommended that users examine the thermodynamic deck before using the program to determine whether complexes, solids, redox reactions, etc., in which they are interested are included in the data. Users are encouraged to create their own data files to suit their own needs. The process of listing, copying, and using an independent data deck is described in Section V-B, page 40.

Figure 17. Examples of thermodynamic data cards.



1. Metals and ligands

Examples of the metal-ligand header card (1), a metal card (2), and a ligand card (3) are shown in Figure 17, page 36. Card (1) says the thermodynamic deck includes information on 35 metals and 59 ligands. Card (2) says metal 23 (Be^{2+} from Table 1, page 45) has a charge of +2, an ionic radius of 0.35 Å, and an atomic weight of 9.102 grams/mole. Sample card (3) says ligand 9 (PO_4^{3-}) has a charge equal to -3, ionic radius of 1.0 Å (if ionic radius is unknown assume 1.0 Å) and a molecular weight of 94.98 grams/mole.

If the user wishes to add more metals or ligands to the deck, this may be done by increasing the numbers on the header card and adding cards for metals 35 to 49 and ligands 59 to 89. Metals and ligands should <u>not</u> be renumbered or rearranged in the data file or they will be labeled incorrectly in the program output. Added metals and ligands will be labeled only as, for example, M37 and L69 in the output unless the program is modified.

2. Complexes and solids

The next card (4) in Figure 17, page 36, after the metal and ligand cards gives the total number of data lines to follow for solids and complexes between the available metals and ligands, the negative log of the ionization constant for water, and 10 log K for the reaction:

$$2H^+ + CO_3^{2-} = CO_2(g) + H_2O \qquad (16)$$

specifically, card (4) in Figure 17 says:

803 lines of data exist for complexes and solids,

$$K_W = (H^+)(OH^-) = 10^{-14}, \text{ and} \qquad (17)$$

$$pCO_2 \,/\, (H^+)^2(CO_3^{2-}) = 10^{18} \qquad (18)$$

The solid and complex cards tell what solids and complexes can exist between a given metal and ligand. These solids and complexes are identified in the program by the metal and the ligand they contain and their order in the line of data for that metal-ligand pair, i.e. as 1,

2, or 3 for the first, second, or third possible solid and as 1 through 6 for the first through sixth complexes. The stoichiometry of the solids and complexes is given in the thermodynamic data and in some of the program outputs.

Two examples of card (5) are shown. The first of these cards reads: metal 9 (Cu^{2+}) and ligand 9 (PO_4^{3-}) form a solid with log K = +37.7 (log K_{sp} = -37.7) containing 3 Cu^{2+}, 2 PO_4^{3-}, and no H^+ or OH^-. Thus

$$3\ Cu^{2+} + 2\ PO_4^{3-} = Cu_3(PO_4)_2\ (s) \qquad K = 10^{37.7} \qquad (19)$$

Cu^{2+} and PO_4^{3-} also form two complexes as follows:

$$Cu^{2+} + PO_4^{3-} + H^+ = CuHPO_4 \qquad K = 10^{16.0} \qquad (20)$$

$$Cu^{2+} + PO_4^{3-} + 2\ H^+ = CuH_2PO_4^+ \qquad K = 10^{21.3} \qquad (21)$$

The second data card says metal 9 (Cu^{2+}) and ligand 99 (OH^-) form a solid with 1 Cu^{2+} and 2 OH^- with log K = -8.3. This reaction is not written with OH^- so,

$$Cu^{2+} + 2\ H_2O = Cu(OH)_2\ (s) + 2\ H^+ \qquad K = 10^{-8.3} \qquad (22)$$

Similarly for the complex,

$$Cu^{2+} + H_2O = CuOH^+ + H^+ \qquad K = 10^{-7.9} \qquad (23)$$

See Section V-C, page 41, for further detail regarding K.

In these solid and complex cards (5), additions, deletions, or modifications may be made on any card with no other changes in the data deck. Also a line of data may be deleted or added and in that instance the total number of solid and complex lines in the data deck must be corrected on the header card (4).

3. Redox equations

The number of redox reactions available follows the solid and complex data and is given on card (6). Each of these reactions is described on a redox card (7). The redox reactions currently on file are given in Table 2, page 46.

For example, card (6) in Figure 17, page 36, says 24 redox reactions are on file. Four examples of redox reactions are shown as card

(7), one for each type as given in field 4. The first card (7) specifies that the first redox reaction (field 1) is of type -10 (field 4), oxidation or reduction, with metal 6 (Fe^{3+}) (field 2) transformed to metal 7 (Fe^{2+}) (field 3), with consumption of 1 electron (field 5) and no H^+ (field 6). Log K is 13 (field 7).

$$Fe^{3+} + e^- = Fe^{2+} \qquad K = (Fe^{2+})/(Fe^{3+})(e^-) = 10^{13} \quad (24)$$

In the second card (7) reaction 2 is of type -2, metal 8 (Mn^{2+}) and ligand 99 (OH^-) form a solid, 2 electrons, and 4 H^+. The solid contains 1 Mn and no OH^- (fields 8 and 9) so OH^- is not really involved. The reaction is:

$$Mn^{2+} + 2H_2O = MnO_2(s) + 4\ H^+ + 2\ e^- \qquad K = 10^{-42.0} \quad (25)$$

In the third card (7) reaction 4 is of type 3 so metal 14 (Hg^{2+}) and ligand 99 form a complex consuming 2 electrons and unaffected by H^+. Two Hg^{2+} are involved and OH^- is again not used. Thus,

$$2\ Hg^{2+} + 2\ e^- = Hg_2{}^{2+} \qquad K = 10^{30.7} \quad (26)$$

In the final redox reaction card shown reaction 9 is of type 10, so ligand 7 (NH_3) is oxidized to ligand 57 (NO_3^-) producing 8 electrons and 9 H^+:

$$NH_3 + 3H_2O = NO_3^- + 8\ e^- + 9\ H^+ \qquad K = 10^{-110} \quad (27)$$

More reactions may be added up to a total of 30. The total number must be corrected on card (6).

4. Mixed Solids

The final data stored in the thermodynamic deck are for mixed solids. Each mixed solid is assigned a number and the total number is recorded on card (8). One card follows for each solid and this card includes the composition, stoichiometry, formation constant, and molecular weight of the solid.

Card (8) in Figure 17, page 36, says 6 mixed solids are available to the program. Cards (9) are two examples of mixed solids available to the program. Mixed solid 2 (field 1) illite is of type 1 (field 2), (an aluminosilicate or clay) and contains 5 (field 7) metal 2, Mg^{2+} (field

3), 12 (field 8) metal 4, K^+ (field 4), no other metals (only 50 in fields 5 and 6), 20 OH^- (field 11), 46 Al^{3+} (field 13) and 70 $SiO_2(OH)_2^{2-}$ field 14). Thus the mixed solid is $Mg_5K_{12}Al_{46}(SiO_2(OH)_2)_{70}(OH)_{20}$, or 1/20 of this as shown in Table 3, and the molecular weight is 7678.40 and log K = 1387.4. The second mixed solid shown (5, field 1), is of type 0 (field 2) and contains 5 (field 7) metal 15, Pb^{2+} (field 3), 3 (field 9) ligand 9, PO_4^{3-} (field 5), and 1 (field 10) ligand 3, Cl^- (field 6). This solid is $Pb_5(PO_4)_3Cl$. The formation constant is $10^{80.4}$ and its molecular weight is 1356.83 grams/mole.

More mixed solid cards may be added to a total of 20. The mixed solid header card (8) must be changed if other mixed solids are added.

V-B. ACCESS TO THE THERMODYNAMIC DATA FILE

All users should obtain a listing of the thermodynamic data file, MREHT. This can be done by the following step:

(log on to WCC)

PRINT CN.EPABDJ.CPR1.MREHT,ROUTE=REMOTENN

where NN is the user's terminal number.

Some users will want to modify the thermodynamic data as described in Section V-A, page 35. To create a different thermodynamic file for personal use the following steps can be taken:

(log on to WCC)

LOAD CN.EPABDJ.CPR1.MREHT

(modify data file as desired)

PRINT *,ROUTE=REMOTENN

SAVE .NEWNAME

where NEWNAME is a name assigned to the newly created file.

In order to use the new data file with REDEQL.EPA replace

DSN=CN.EPABDJ.CPR1.MREHT

with DSN=CN.EPAIII.AAAA.NEWNAME,

where III = customer identification

AAAA = account number

in the seventh control card shown in Section III-B, page 15.

V-C. PREPARATION OF DATA FOR SOLIDS AND COMPLEXES FOR ENTRY INTO THE THERMODYNAMIC DATA FILE.

To enter a solid or complex into the thermodynamic data file one must know the metal and ligand composition of the solid or complex and be certain these are given in cards (2) and (3) of the thermodynamic deck. The formation reaction for the solid or complex must be written and K (the equilibrium constant) for that reaction must be ascertained. Often, K for the formation reaction is not known, so it must be determined from some related parameter. OH^- can not be used in any reaction but must be replaced by H_2O and H^+, because H^+ and OH^- are not independent species but are related by the ion product of water, K_w.

Consider the complex $CdOH^+$. For this complex the formation reaction is written:

$$Cd^{2+} + H_2O = CdOH^+ + H^+ \qquad (28)$$

Any of the following data might be known for the species $CdOH^+$

(a) $K = \dfrac{(CdOH^+)\,(H^+)}{(Cd^{2+})}$, the equilibrium constant for the formation reaction required by the program at infinite dilution.

(b) $K' = \dfrac{(CdOH^+)}{(Cd^{2+})(OH^-)}$, the equilibrium constant for the formation reaction including OH^-, $Cd^{2+} + OH^- = CdOH^-$ (29)

(c) ΔG° for the reaction (28) above, where ΔG° is the free energy of reaction.

(d) $\Delta G^{\circ\prime}$ for the reaction (29) above.

(e) ΔG°_f for $CdOH^+$, the free energy of formation of $CdOH^+$ which is the change in free energy when $CdOH^+$ is formed from elements in their standard states:

$$Cd(s) + 1/2\ O_2(g) + 1/2\ H_2(g) = CdOH^+ + e^- \qquad (30)$$

the program needs log K. The other quantities, (b) through (e) can be readily converted to K. The equations relating each of these to K are shown below.

For (b), $K = K'K_w$ where $K_w = (H^+)(OH^-) = 10^{-14}$ (31)

For (c) $\log K = -\frac{\Delta G^\circ}{2.303RT}$ where $R = 1.987$ cal/mole-deg, $T = 298.16^\circ K$ (32)

For (d), $\log K' = -\frac{\Delta G^{\circ\prime}}{2.303RT}$ where R and T are as above. (33)

and

$$\log K = \log K' + \log K_w \quad (34)$$

For (e) either ΔG° or $\Delta G^{\circ\prime}$ can be calculated provided ΔG_f° is known, where ΔG_f° is the change in free energy when $CdOH^+$ or any other species is formed from elements in their standard states (equation 30). For any reaction, ΔG° is the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants. Thus for the reaction shown in equation (28), the change in free energy is:

$$\Delta G^\circ = \Delta G^\circ_{f,CdOH^+} + \Delta G^\circ_{f,H^+} - \Delta G^\circ_{f,Cd^{2+}} - \Delta G^\circ_{f,H_2O} \text{ where } \Delta G^\circ_{f,H^+} = 0 \quad (35)$$

and the values for ΔG_f°, reactants are obtained from tables (e.g., references 10 and 11). Then determine K from equation (32).

As a second example of free energy of reaction $\Delta G^{\circ\prime}$ for reaction (29) is determined by equation (36),

$$\Delta G^{\circ\prime} = \Delta G^\circ_{f,CdOH^+} - \Delta G^\circ_{f,Cd^{2+}} - \Delta G^\circ_{f,OH^-} \quad (36)$$

where the values for ΔG_f°, reactants are obtained as above. Then determine K using equations (33) and (34).

Any equation written in reverse from those given here will have the opposite sign for the change in free energy and K will be the reciprocal of that required by the program.

1. A reference might give

$$\Delta G^\circ_{f,CdOH^+} = -62.4 \text{ kcal/mole}$$

Proceeding as in (e) above, reaction (28) may be written. From a tabulation (10, 11)

$$\Delta G^\circ_{f,Cd^{2+}} = -18.54$$

$$\Delta G^\circ_{f,H_2O} = -56.69$$

$$\Delta G^\circ_{f,H^+} = 0$$

Subtraction of the free energy of formation of the reactants from the energy of the product (equation 35)

$$\Delta G^\circ = -62.4 + 0 - (-18.54) - (-56.69)$$

$$= 12.83 \text{ kcal/mole}$$

$$= 12830 \text{ cal/mole}$$

and then from equation (32)

$$\log K = -\frac{12830}{(2.303)(1.987)(298.16)}$$

$$\log K = -9.4$$

2. Or some reference might give $K' = 10^{4.59}$ for reaction (29) then proceeding as for (b) above using equation (31)

$$K = (10^{4.59})(10^{-14})$$

$$K = 10^{-9.4}$$

and

$\log K = -9.4$ as in the first example.

After log K has been determined, the data can be inserted in the thermodynamic data file according to the format in Table 6, page 55.

Data for solids are similarly treated. Solubility products are often given and these are the reciprocal of formation constants.

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Table 1. Reference Numbers for Metals and Ligands

Metals

1.	Ca^{2+}	8.	Mn^{2+}	15.	Pb^{2+}	22.	Li^{+}	29.	Ce^{3+}
2.	Mg^{2+}	9.	Cu^{2+}	16.	Co^{2+}	23.	Be^{2+}	30.	Au^{+}
3.	Sr^{2+}	10.	Ba^{2+}	17.	Co^{3+}	24.	Sc^{3+}	31.	Th^{4+}
4.	K^{+}	11.	Cd^{2+}	18.	Ag^{+}	25.	TiO^{2+}	32.	UO_2^{2+}
5.	Na^{+}	12.	Zn^{2+}	19.	Cr^{3+}	26.	Sn^{2+}	33.	Cu^{+}
6.	Fe^{3+}	13.	Ni^{2+}	20.	Al^{3+}	27.	Sn^{4+}	34.	CH_3Hg^{+}
7.	Fe^{2+}	14.	Hg^{2+}	21.	Cs^{+}	28.	La^{3+}	50.	H^{+}

Ligands*

1.	CO_3^{2-}	13.	$S_2O_3^{2-}$	25.	$GLUT^{2-}$	37.	ASP^{-}	49.	SO_3^{2-}
2.	SO_4^{2-}	14.	CN^{-}	26.	PIC^{-}	38.	SER^{-}	50.	SCN^{-}
3.	Cl^{-}	15.	AC^{-}	27.	NTA^{3-}	39.	ALA^{-}	51.	NH_2OH
4.	F^{-}	16.	$ACAC^{-}$	28.	$EDTA^{4-}$	40.	TYR^{2-}	52.	MoO_4^{2-}
5.	Br^{-}	17.	CIT^{3-}	29.	$DCTA^{4-}$	41.	MET^{-}	53.	WO_4^{2-}
6.	I^{-}	18.	OX^{2-}	30.	$CYST^{2-}$	42.	VAL^{-}	54.	AsO_4^{3-}
7.	NH_3^0	19.	SAL^{2-}	31.	NOC^{3-}	43.	THR^{-}	55.	HVO_4^{2-}
8.	S^{2-}	20.	$TART^{2-}$	32.	$PHTH^{2-}$	44.	PHE^{-}	56.	SeO_3^{2-}
9.	PO_4^{3-}	21.	EN^0	33.	ARG^{-}	45.	ISO^{-}	57.	NO_3^{-}
10.	$P_2O_7^{4-}$	22.	DIP^0	34.	ORN^{-}	46.	LEU^{-}	58.	$DTPA^{4-}$
11.	$P_3O_{10}^{5-}$	23.	$SUSAL^{3-}$	35.	LYS^{-}	47.	PRO^{-}	99.	OH^{-}
12.	$SiO_2(OH)_2^{2-}$	24.	GLY^{-}	36.	HIS^{-}	48.	$B(OH)_4^{-}$		

*AC = acetate
ACAC = acetylacetate
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = ethylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLUT = glutamate
PIC = picolinate
NTA = nitrilotriacetate
EDTA = ethylenediaminetetraacetate
DCTA = 1,2-diaminocyclohexane-tetracetate
CYST = cysteine
NOC = nocardamine (desferri-ferrioxamine)
PHTH = phthalate
ARG = arginine
ORN = ornithine
LYS = lysine
HIS = histidine
DTPA = diethylenetriaminepentaacetate
ASP = aspartate
SER = serine
ALA = alanine
TYR = tyrosine
MET = methionine
VAL = valine
THR = threonine
PHE = phenylalanine
ISO = isoleucine
LEU = leucine
PRO = proline

Table 2. Redox Reactions: Reference number, type, and equilibrium constant

Reference Number	Reaction Type	Reaction	Log K
1	-10	$Fe^{3+} + e- \rightarrow Fe^{2+}$	13.0
2	-2	$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e-$	-42.0
3	-2	$Hg^{2+} + 2e- \rightarrow Hg(liq)$	28.7
4	3	$2Hg^{2+} + 2e- \rightarrow Hg_2^{2+}$ (aq)	30.7
5	-2	$Pb^{2+} + 2H_2O \rightarrow PbO_2(s) + 4H^+ + 2e-$	-49.2
6	-10	$Co^{2+} \rightarrow Co^{3+} + e-$	-31.6
7	3	$CO_3^{2-} + 6H^+ + 4e- \rightarrow CH_2O(aq) + 2H_2O$	13.2
8	10	$SO_4^{2-} + 8H^+ + 8e- \rightarrow S^{2-} + 4H_2O$	20.0
9	10	$NH_3(aq) + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e-$	-110.0
10	1	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e-$	-60.1
11	-10	$Sn^{2+} \rightarrow Sn^{4+} + 2e-$	-5.1
12	-2	$Fe^{2+} + 2S^{2-} \rightarrow FeS_2(s) + 2e-$	45.3
13	-2	$3Fe^{3+} + 4H_2O + e- \rightarrow Fe_3O_4(s) + 8H^+$	6.4
14	-3	$3Mn^{2+} + 4H_2O \rightarrow Mn_3O_4(s) + 8H^+ + 2e-$	-61.7
15	-1	$Mn^{2+} + 2H_2O \rightarrow MnO(OH)(s) + 3H^+ + e-$	-25.7
16	4	$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14\ H^+ + 6e-$	-135.2
17	5	$Cr^{3+} + 4H_2O \rightarrow HCrO_4^- + 7H^+ + 3e-$	-68.4
18	6	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e-$	-74.9
19	-1	$S^{2-} \rightarrow S(s) + 2e-$	16.2
20	3	$4S^{2-} \rightarrow S_4^{2-} + 6e-$	71.6
21	4	$5S^{2-} \rightarrow S_5^{2-} + 8e-$	87.1
22	-10	$Cu^+ \rightarrow Cu^{2+} + e-$	-2.6
23	-1	$Cu^+ + e- \rightarrow Cu(s)$	8.8
24	-1	$2NO_3^- + 12H^+ + 10e- \rightarrow N_2(g) + 6H_2O$	208.9

Table 3. Mixed Solids: Reference number, type, and equilibrium constant

Reference Number	Reaction Type	Reaction	Log K
1	1	$5\ Mg^{2+} + 2\ Al^{3+} + 3\ SiO_3^{2-} + 9\ H_2O \rightarrow Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ H^+$	-4.9
2	1	$5\ Mg^{2+} + 12\ K^+ + 46\ Al^{3+} + 70\ SiO_3^{2-} + 30\ H_2O \rightarrow 20(K_{.6}Mg_{.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2) + 20\ H^+$	1387.4
3	1	$K^+ + Al^{3+} + 3\ SiO_3^{2-} + 2\ H^+ \rightarrow KAlSi_3O_8 + H_2O$	67.1
4	1	$Na^+ + 7\ Al^{3+} + 11\ SiO_3^{2-} + 3H_2O \rightarrow 3(Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2)$	232.3
5	0	$Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-} \rightarrow CaMg(CO_3)_2$	19.7
6	0	$5\ Pb^{2+} + 3\ PO_4^{3-} + Cl^- \rightarrow Pb_5(PO_4)_3Cl$	80.4

NAME OF MIXED SOLIDS

Reference Number	Name	As Appears on Printout
1	CHLORITE	CHLORITE
2	ILLITE	ILLITE
3	MICROCLINE	MICCLINE
4	NA-MONTMORILLONITE	NA-MONT
5	DOLOMITE	DOLOMITE
6	$Pb_5(PO_4)_3Cl$	PBPO4CL

Table 4
Program Input Cards:
Card sequence, format, and data required

Card type	Field	Card columns	Description
(1)	Program header card: 1 card, Format 17I3. All blanks are read as zeros.		
	1	1-3	Number of metals including H^+. ($\leq$ 20).
	2	4-6	Number of ligands including OH^-. ($\leq$ 30).
	3	7-9	Number of cases to be considered. ($\leq$ 10). A case consists of total concentrations for a group of metals and ligands and pH or TOTH for that set of concentrations. Different pCO_2, pE, and pN_2, may also be specified. One or more of the above parameters may be varied from case to case. The number of metals or ligands cannot be changed although concentrations may be vanishingly small.
	4	10-12	Solid phases to consider (see Section III-E, page 21). -1 means no solids may precipitate even when the solution is supersaturated. 0 means no solids are imposed (assumed to be in contact with the solution) but any solid may precipitate if the solution is saturated with respect to it. N, where 0 < N $\leq$ 13, is the sum of those solids imposed and those not allowed to precipitate. If N in field 4, card (10) is required.
	5	13-15	Blank
	6	16-18	Blank
	7	19-21	pH, calculated or fixed? 0 means pH is specified for each case. 1 means the program will compute pH for each case. Note: If this field is 1, TOTH data card (6) is required.
	8	22-24	Redox reactions. 0 means no redox reactions considered. 1 means the program will include redox reactions. Note: If this field is 1, an electron activity card (8) and a redox reaction card (11) are required and a pN_2 card (9) is required if NO_3^- is present.
	9	25-27	Mixed solids. 0 means no mixed solids considered. 1 means some mixed solids considered. Note: If this field is 1, a mixed solids card (12) is required.
	10	28-30	Ionic strength. 0 means the user specifies the ionic strength for the computer run (same value for all cases). 1 means the program will compute the ionic strength for each case.

Card type	Field	Card columns	Description
			Fields 11 thru 16 merely suppress or increase output. They are generally 0 or left blank. See Section IV, page 26, for a description of the output routines.
	11	31-33	Selects interaction intensity and/or capacity output routine. 0 means no output. 1 means interaction capacities computed and printed. 2 means interaction intensities computed and printed. 3 means both are printed.
	12	34-36	0 means output routine for case progress is used. 1 means suppressed.
	13	37-39	0 means output routine for complex concentrations is used. 1 means suppressed.
	14	40-42	0 means output routine for speciation of the ions is used. 1 means suppressed.
	15	43-45	0 means output routine for primary distribution of species is used. 1 means suppressed.
	16	46-48	0 means output routine for verification of thermodynamic data is used after each case when ionic strength is calculated. 1 means suppressed after each case.
	17	49-51	Concentration units. 0 means the input data concentration will be expressed as $-\log_{10}$(molar concentration) or -log M. 1 means the input data will be expressed in mg/l (approximately ppm). These units will also be used in the output routines for input data verification and case progress.

(2) Ionic strength card: 1 card, Format E7.2

1	1-7	Fixed or guessed ionic strength in molar units, (moles/l). See Section III-C, page 15, and field 10 in program header card.

(3) Metal Cards: # cards = # metals on the header card minus one. No card required for H^+. Format is I2,2X,11(1X,F5.2) for molar concentration. Format is I2,2X,11E6.2 for mg/l concentrations. Column numbers enclosed in parenthesis indicate mg/l format.

1	1-2	Reference number of metal. See Table 1, page 45.

Card type	Field	Card Columns	Description
	2		Guess of the free concentration of the metal for the first case. (See discussion in Section III-A, page 10.)
		6-10	Use -log M for molar concentration. If 0, program assumes a value of 8.
		(5-10)	Use mg/l for concentration. Must be $\geq 10^{-14}$.

The following fields are for the total concentration of the metals for up to ten cases. All cases must be in the same units.

3	12-16	First case. Use -log M for molar concentration. If the first case is 0, program assumes 1M total concentration. If any subsequent value is 0, the value from the previous case is used.
	(11-16)	First case. Use mg/l for total concentration. Value for the first case must be $\geq 10^{-14}$. If any subsequent value is 0, the value from the previous case is used.
4	18-22 (17-22)	Second case. Description for this case and the remaining cases is the same as for the first case.
5	24-28 (23-28)	Third case.
6	30-34 (29-34)	Fourth case.
7	36-40 (35-40)	Fifth case.
8	42-46 (41-46)	Sixth case.
9	48-52 (47-52)	Seventh case.
10	54-58 (53-58)	Eight case.
11	60-64 (59-64)	Ninth case.
12	66-70 (65-70)	Tenth case.

(4) Ligand cards: # cards = # ligands on the header card minus one. No card required for OH^-. Format I2,2X,11(1X,F5.2) is for molar concentration. Format I2,2X,11E6.2 is for mg/l concentrations. Column numbers enclosed in parenthesis indicate mg/l format.

1	1-2	Reference number of ligand. See Table 1, page 45.
Field, column, and case numbers the same as card (3).		Description identical to card (3) except for ligand instead of metal concentrations.

Card type	Field	Card Columns	Case	Description
(5)	pH card: 1 required, Format 4X,10(1X,F5.2)			
	1	6-10	1	If pH is imposed (0 in field 7 of program header card), give pH for each case. If pH is calculated (1 in field 7), give a guess of pH for each case. If first case is 0, program assumes a value of 8. If any subsequent case is 0, the value from the previous case is used.
	2	12-16	2	
	3	18-22	3	
	4	24-28	4	
	5	30-34	5	
	6	36-40	6	
	7	42-46	7	
	8	48-52	8	
	9	54-58	9	
	10	60-64	10	
(6)	TOTH card: 1 card, used only if pH calculated (field 7 of the program header card = 1), Format 10E7.2			
	1	1-7	1	TOTH = $\Sigma H^+ - \Sigma OH^-$. See Section III-D, page 17, for calculation. A value must be given for each case, as a molar concentration (not -log M). A zero or blank means zero value for that case.
	2	8-14	2	
	3	15-21	3	
	4	22-28	4	
	5	29-35	5	
	6	36-42	6	
	7	43-49	7	
	8	50-56	8	
	9	57-63	9	
	10	64-70	10	
(7)	Partial pressure of CO_2 card: 1 card used only if ligand 1, CO_3^{2-}, is included, Format 10F5.2.			
	1	1-5	1	Partial pressure of CO_2, pCO_2, is given as -log (pressure in atmospheres). If 0 for the first case, no partial pressure is allowed. If any subsequent value is 0, value from the preceding case is used. (Normal partial pressure is $10^{-3.5}$ atm.) Caution: See discussion in Section III-F, page 22.
	2	6-10	2	
	3	11-15	3	
	4	16-20	4	
	5	21-25	5	
	6	26-30	6	
	7	31-35	7	
	8	36-40	8	
	9	41-45	9	
	10	46-50	10	

Card type	Field	Card Columns	Description
(8) Electron activity card: 1 card used only if redox reactions considered (field 8 of the program header card = 1), Format 10F5.2.			
	1	1-5	Case 1 -log (electron activity), pE, must be given for each case. 0 means 0. Typical values range from -4 (reducing) to 12 (oxidizing).
	Field, column, and case numbers the same as for card (7)		
(9) Partial pressure of N_2 card: 1 card used only if redox reactions considered (field 8 of the program header card = 1) and if NO_3^- (ligand 57) is included, Format 10F5.2			
	1	1-5	Case 1 -log (partial pressure of N_2), pN_2, where the pressure is in atmospheres and is given for each case. If 0 for the first case, no partial pressure is allowed. If any subsequent value is 0, value from previous case is used. (Normal partial pressure is $10^{-.1}$ atm.)
	Field, column, and case numbers the same as for card (7)		
(10) Solids card: 1 card used only if solids are imposed and/or not allowed to precipitate (field 4 of the program header card > 0), Format 39I2			
	1	1-2	Reference number of metal in solid A. See Table 1, page 45.
	2	3-4	Reference number of ligand in solid A. See Table 1.
	3	5-6	1, 2, or 3 depending on whether A is the first, second or third solid listed in the thermodynamic data file. If this number is positive, the solid is imposed. If this number is negative, the solid is not allowed to precipitate.
	4	7-8	Same set of 3 parameters in six columns for up to 13 solids.
	5	9-10	Solid B.
	6	11-12	
	7	13-14	
	8	15-16	Solid C.
	9	17-18	
	Etc.		

Card type	Field	Card column	Description
(11)	Redox reaction card: 1 card used only if redox reactions considered, (field 8 of program header card = 1), Format 20I2		
	1	1-2	First redox reaction considered. Enter reaction reference number from Table 2, page 46, or from the thermodynamic data file. Up to 20 reactions, two columns/reaction.
	2	3-4	Second redox reaction.
	3	5-6	
	4		
	Etc.		
(12)	Mixed solids card: 1 card used only if mixed solids considered (field 9 of the program header card = 1), may be blank, Format 20I4		
	1	1-4	Mixed solid reference number from Table 3, page 47, or from the thermodynamic data file. If the number is positive the solid is imposed. If the number is negative the solid is not allowed to precipitate. A mixed solid whose number is not given is allowed to precipitate. Up to 20 solids, 4 columns/solid
	2	5-8	Second mixed solid.
	3	9-12	
	4		
	Etc.		

Table 5
Figure References for Output Routines

Text number	Routine name	Figure
1	Thermodynamic input data for verification	6a, 6g, 9g, 10b, 11b, 12b, 13b
2	Input data	6b, 9b, 11c, 12c, 14b
3	Case progress	6c, 7b, 9c, 9e, 9h, 10c, 11d, 12d, 12e, 12f, 12g, 13c, 14c
4	Concentration of complexes	6d
5	Speciation of metals and ligands	6e
6	Primary distribution of metals and ligands	6f, 9d, 9f, 9i, 10d, 11e, 13d

Table 6
Thermodynamic Data Deck:
Card sequence, format, and data required

Card type	Field	Card columns	Description
(1)	Metal and ligand header card: 1 card, Format 2I3		
	1	1-3	The number of metals including hydrogen for which data are available to the program.
	2	4-6	The number of ligands including hydroxide for which data are available to the program.
(2)	Metal cards: # cards = # metals given on header card, (1), Format I2,I3,F7.2,F9.3		
	1	1-2	Reference number of metal. See Table 1, page 45.
	2	3-5	Charge of the metal.
	3	6-12	Ionic radius of metal in Angstroms. Used only in adsorption, use 1.0 if unknown.
	4	13-21	Molecular weight of metal in grams/mole.
(3)	Ligand cards: # cards = # ligands given on header card, (1), Format I2,I3,F7.2,F9.3		
	1	1-2	Reference number of ligand. See Table 1, page 45.
	2	3-5	Charge of ligand, including sign.
	3	6-12	Ionic radius of ligand in Angstroms. Used only in adsorption, use 1.0 if unknown.
	4	13-21	Molecular weight of ligand in grams/mole.
(4)	Solid and complex header card: 1 card, Format I5,F5.2,F5.1		
	1	1-5	Number of metal-ligand solid/complex cards to follow.
	2	6-10	-log of the ionization constant of water = 14 at 0 ionic strength, T = 25°C.
	3	11-15	10 log K of the equilibrium constant for the reaction: $2H^+ + CO_3^{2-} \rightarrow CO_2(g) + H_2O$
(5)	Solid and complex cards: # cards = # given on header card (4), Format 2I2,9(I4,2I1,12)		
	1	1-2	Reference number of metal.
	2	3-4	Reference number of ligand combined with above metal.
	3	5-8	10 log K where K is the formation constant of a solid formed from the above metal, ligand, and hydrogen or hydroxide.
	4	9	Stoichiometric coefficient of the metal in the first solid.

Card type	Field	Card columns	Description
	5	10	Stoichiometric coefficient of the ligand in the first solid.
	6	11-12	Stoichiometric coefficient of hydrogen (negative if hydroxide) in the first solid. Zero if neither present.
	7	13-16	
	8	17	Same as Fields 3 thru 6, except for second solid.
	9	18	
	10	19-20	
	11	21-24	
	12	25	Same as Fields 3 thru 6, except for third solid.
	13	26	
	14	27-28	
	15	29-32	10 log K where K is the formation constant of a complex from the metal and ligand given in combination with hydrogen or hydroxide.
	16	33	Stoichiometric coefficient of the metal in the first complex
	17	34	Stoichiometric coefficient of the ligand in the first complex.
	18	35-36	Stoichiometric coefficient of hydrogen (negative if hydroxide) in the first complex. Zero if neither present.
	19	37-40	
	20	41	Same as Fields 15 thru 18, except for a second
	21	42	complex.
	22	43-44	
	23	45-48	
	24	49	Same as Fields 15 thru 18, except for a third
	25	50	complex.
	26	51-52	
	27	53-56	
	28	57	Same as Fields 15 thru 18, except for a fourth
	29	58	complex.
	30	59-60	
	31	61-64	
	32	65	Same as Fields 15 thru 18, except for a fifth
	33	66	complex.
	34	67-68	
	35	69-72	
	36	73	Same as Fields 15 thru 18, except for a sixth
	37	74	complex.
	38	75-76	

Card type	Field	Card columns	Description

(6) Redox reaction header card: 1 card, Format I5

1	1-5	Number of redox reactions ($\leq$30)

(7) Redox reaction cards: # cards = # given on header card (6), Format 9I5,A8

1	1-5	Arbitrary sequential number assigned to the redox reaction. See Table 2, page 46. The last reaction number must be assigned to: $2NO_3^- + 12H^+ \rightarrow N_2(g) + 6H_2O - 10e^-$
2	6-10	Reference # of: reacting metal / metal produced
3	11-15	Reference # of: metal / ligand
4	16-20	Reaction type: reacting ligand / ligand produced

Reaction type	reacting metal / metal produced	metal / ligand	reacting ligand / ligand produced
-10			10
-9 to -1		1 to 9	

-10 is a metal oxidized/reduced to another metal ± e-.
-9 to -1 is a metal + ligand forming a solid ± e-.
1 to 9 is a metal + ligand forming a complex ± e-.
10 is a ligand oxidized/reduced to another ligand ± e-.

5	21-35	Number of e^- produced (negative if consumed).
6	26-30	Number of H^+ consumed (negative if produced).
7	31-35	10 log K for the reaction as written.
8	36-40	Stoichiometric coefficient of ion given in field 2. Zero if reaction type ± 10 or metal 50.
9	41-45	Stoichiometric coefficient of ion given in field 3. Zero if reaction type ± 10 or ligand 99.
10	46-53	Name of the reaction, up to 8 alphanumeric characters.

(8) Mixed solid header card: 1 card, Format I4

1	1-4	Number of mixed solids for which data are available to the program ($\leq$ 20).

(9) Mixed solid cards: # cards = # given on header card (8), Format 11I4,I6,2I3,A8,F7.2

1	1-4	Arbitrary sequential number assigned to the mixed solid. See Table 3, page 47.
2	5-8	Reaction type: 0 if solid contains up to 2 metals and 2 ligands in addition to possible H^+ or OH^-. 1 if solid contains up to 4 metals in addition to Al^{3+} and $SiO_2(OH)_2^{2-}$.
3	9-12	Reference number of first metal.
4	13-16	Reference number of second metal. 50 if no second metal.
5	17-20	Reference number of third metal for reaction type 1. Reference number of first ligand for reaction type 0. 50 if no third metal.

Card type	Field	Card column	Description
	6	21-24	Reference number of fourth metal for reaction type 1. Reference number of second ligand for reaction type 0. 50 if no fourth metal. 99 if no second ligand.
	7	25-28	Stoichiometric coefficient for ion in field 3.
	8	29-32	Stoichiometric coefficient for ion in field 4. Zero if no second metal.
	9	33-36	Stoichiometric coefficient for ion in field 5. Zero if nc third metal.
	10	37-40	Stoichiometric coefficient for ion in field 6. Zero if no fourth metal or second ligand.
	11	41-44	Number of hydrogens in the solid (negative if hydroxide present). Do not count OH^- of $SiO_2(OH)_2^{2-}$
	12	45-50	10 log K where K is the formation constant of the reaction as written. See Table 3.
	13	51-53	Number of Al^{3+} ions for type 1 reaction. Zero for type 0 reaction.
	14	54-56	Number of $SiO_2(OH)_2^{2-}$ ions for type 1 reaction. Zero for type 0 reaction.
	15	57-64	Name of the mixed solid.
	16	65-71	Molecular weight of the mixed solid in grams/mole.

COMPUTER PRINTOUT

Figure 6
Output for a simple case

6a.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID						COMPLEXES															
			1		2		3		1		2		3		4		5		6				
1	1	711	1 1 0		0 0 0 0		0 0 0 0		181	1 1 0	1048	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
1	3	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
1	99	-2234	1 0-2		0 0 0 0		0 0 0 0		-1257	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
2	1	421	1 1 0		0 0 0 0		0 0 0 0		201	1 1 0	1048	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
2	3	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
2	99	-1684	1 0-2		0 0 0 0		0 0 0 0		-1157	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
5	1	0	0 0 0		0 0 0 0		0 0 0 0		60	1 1 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
5	3	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
5	99	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
6	1	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
6	3	0	0 0 0		0 0 0 0		0 0 0 0		51	1 1 0	61	1 2 0	-47	1 3 0	0 0 0 0		0 0 0 0		0 0 0 0				
6	99	-401	1 0-3		0 0 0 0		0 0 0 0		-286	1 0-1	-723	1 0-2	-2408	1 0-4	-304	2 0-2	0 0 0 0		0 0 0 0				
50	1	-4	0 1 2		0 0 0 0		0 0 0 0		968	0 1 1	1575	0 1 2	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
50	3	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				
50	99	0	0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0				

6b.

INPUT DATA

THESE COMPUTATIONS INVOLVE 5 METALS, 3 LIGANDS, 16 COMPLEXES AND 6 POSSIBLE SOLIDS.

IONIC STRENGTH= 0.1110000E 01

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	TOTCC
CA	1	1.000	1.000	
MG	2	1.300	1.300	
NA	5	0.300	0.300	
FE3	6	2.000	2.000	
LIGAND	#INMAT	GUESS	TOTCC 1	TOTCC
CO3-	1	1.000	0.700	
CL	3	0.280	0.280	
PH GUESS 1		8.000		
TOTH			0.10E 00	

6c.
CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 36

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 39

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 48

NUMBER OF ITERATIONS= 51

IONIC STRENGTH= 6.3052237E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.410

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	2.6781571E-03	2.57216	1.0000002E-01	1.00000	-1.2338161E-05
MG	3.7081733E-02	1.43084	5.0118871E-02	1.30000	1.4649195E-06
NA	5.0112247E-01	0.30006	5.0118738E-01	0.30000	-2.9700459E-08
FE3	7.4247097E-16	15.12932	1.0000009E-02	2.00000	0.0
CO3-	3.7339152E-05	4.42784	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	2.3611384E-15
TOTH	3.8924327E-07	6.40978	9.9999964E-02		1.5623868E-05

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.6370697E-02
FE3	OH	1	1.0000005E-02

6d.

CONCENTRATIONS OF COMPLEXES

CONCENTRATION OF COMPLEX (-LOG M) FOLLOWED BY
STOICHIOMETRY OF THE COMPLEX (METAL, LIGAND, HYDROGEN)

CA	CO3-	5.30	1 1 0	3.03	1 1 1				
CA	OH	8.76	1 0-1						
MG	CO3-	3.96	1 1 0	1.89	1 1 1				
MG	OH	6.62	1 0-1						
NA	CO3-	4.19	1 1 0						
FE3	CL	14.98	1 1 0	15.21	1 2 0	16.59	1 3 0		
FE3	OH	11.63	1 0-1	9.63	1 0-2	13.64	1 0-4	20.49	2 0-2
H	CO3-	1.21	0 1 1	1.57	0 1 2				

6e. SPECIATION OF METALS AND LIGANDS
SUM OF CONCENTRATION OF ALL SPECIES AS -LOG(M)

	FREE MET	CO3-	CL	OH
FREE LIG		4.43	0.28	7.35
CA	2.57	3.03	*****	8.76
MG	1.43	1.88	*****	6.62
NA	0.30	4.19	*****	*****
FE3	15.13	*****	14.77	9.63
HYDROGEN	6.41	1.05	*****	*****

6f.

PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN; BOUND SIGNIFIES COMPLEXED

CA

AS A FREE METAL/ 2.7 PERCENT
BOUND WITH CO3-/ 0.9 PERCENT
IN SOLID FORM WITH CO3-/ 96.4 PERCENT

MG

AS A FREE METAL/ 74.0 PERCENT
BOUND WITH CO3-/ 26.0 PERCENT

NA

AS A FREE METAL/ 100.0 PERCENT

FE3

IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-

IN SOLID FORM WITH CA / 48.3 PERCENT
BOUND WITH MG / 6.5 PERCENT
BOUND WITH H / 44.6 PERCENT

CL

AS A FREE LIGAND/ 100.0 PERCENT

6g.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID 1	SOLID 2	SOLID 3	COMPLEXES 1	COMPLEXES 2	COMPLEXES 3	COMPLEXES 4	COMPLEXES 5	COMPLEXES 6
1	1	700 1 1 0	0 0 0 0	0 0 0 0	170 1 1 0	1038 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	99	-2237 1 0-2	0 0 0 0	0 0 0 0	-1260 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	1	410 1 1 0	0 0 0 0	0 0 0 0	190 1 1 0	1038 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	99	-1687 1 0-2	0 0 0 0	0 0 0 0	-1160 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	1	0 0 0 0	0 0 0 0	0 0 0 0	54 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	3	0 0 0 0	0 0 0 0	0 0 0 0	43 1 1 0	48 1 2 0	-62 1 3 0	0 0 0 0	0 0 0 0	0 0 0 0
6	99	-410 1 0-3	0 0 0 0	0 0 0 0	-291 1 0-1	-732 1 0-2	-2415 1 0-4	-305 2 0-2	0 0 0 0	0 0 0 0
50	1	-10 0 1 2	0 0 0 0	0 0 0 0	963 0 1 1	1568 0 1 2	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0

Figure 7
A case with fixed ionic strength

7b.

CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 36

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 39

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 48

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.413

7a. Input cards

```
(1)   5  3  1  0  0  0  1  0  0  0
(2) 1.11E 0
(3)  1    1.0   1.0
     2    1.3   1.3
     5    0.3   0.3
     6    2.0   2.0
(4)  1    1.0    0.7
     3    0.28  0.28
(5)       8.0
(6) 0.1
(7)  0.0
```

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	2.3719610E-03	2.62489	1.0000002E-01	1.00000	1.1920929E-07
MG	3.6191728E-02	1.44139	5.0118871E-02	1.30000	-4.6641730E-09
NA	5.0112206E-01	0.30006	5.0118738E-01	0.30000	-3.8092362E-08
FE3	5.8841028E-16	15.23033	1.0000009E-02	2.00000	0.0
CO3-	3.2726050E-05	4.48511	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	2.4061286E-15
TOTH	3.8597256E-07	6.41344	9.9999964E-02		-1.6018748E-07

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.6718252E-02
FE3	OH	1	1.0000009E-02

Figure 9
Three cases with fixed pH

9b.

INPUT DATA

THESE COMPUTATIONS INVOLVE 5 METALS, 3 LIGANDS, 16 COMPLEXES AND 6 POSSIBLE SOLIDS.

IONIC STRENGTH= 0.1110000E 01

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

3 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	TOTCC 2	TOTCC 3	TOTCC
CA	1	1.000	1.000	1.000	1.000	
MG	2	1.300	1.300	1.300	1.300	
NA	5	0.300	0.300	0.300	0.300	
FE3	6	2.000	2.000	2.000	2.000	
LIGAND	#INMAT	GUESS	TOTCC 1	TOTCC 2	TOTCC 3	TOTCC
CO3-	1	1.000	0.700	0.700	0.700	
CL	3	0.280	0.280	0.280	0.280	
F I X E D P H			8.000	8.000	4.000	
CO2 PRESSURE			0.0	3.500	0.0	

9a. Input cards

```
(1)   5  3  3  0  0  0  0  0  0  1
(2) 1.11E 0
(3)  1    1.0    1.0
     2    1.3    1.3
     5    0.3    0.3
     6    2.0    2.0
(4)  1    1.0     0.7
     3    0.28   0.28
(5)       8.0    8.0    4.0
(7)  0.0  3.5
```

9c.
CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 14

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 15

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 21

NUMBER OF ITERATIONS= 24

IONIC STRENGTH= 6.2531871E-01

FIXED PH= 8.000 COMPUTED TOTH= 0.6109280E-01

9d.
PRIMARY DISTRIBUTION OF METALS AND LIGANDS -

SPECIES OVER 0.05% SHOWN; BOUND SIGNIFIES COMPLEXED

CA
IN SOLID FORM WITH CO3-/ 99.9 PERCENT

MG
AS A FREE METAL/ 63.8 PERCENT
BOUND WITH CO3-/ 36.2 PERCENT

NA
AS A FREE METAL/ 99.4 PERCENT
BOUND WITH CO3-/ 0.6 PERCENT

FE3
IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-
AS A FREE LIGAND/ 0.9 PERCENT
IN SOLID FORM WITH CA / 50.1 PERCENT
BOUND WITH MG / 9.1 PERCENT
BOUND WITH NA / 1.5 PERCENT
BOUND WITH H / 38.4 PERCENT

CL
AS A FREE LIGAND/ 100.0 PERCENT

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	5.6309786E-05	4.24942	1.0000002E-01	1.00000	0.0
MG	3.1977393E-02	1.49516	5.0118871E-02	1.30000	5.6554200E-08
NA	4.4812007E-01	0.30267	5.0118738E-01	0.30000	-4.4470653E-08
FE3	1.2589660E-20	19.89999	1.0000009E-02	2.00000	0.0
CO3-	1.7758941E-03	2.75058	1.9952637E-01	0.70000	5.9604645E-08
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	4.0037377E-20

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.9914610E-02
FE3	OH	1	1.0000009E-02

9e.
CASE NUMBER 2

CASE PROGRESS

NUMBER OF ITERATIONS= 26

IONIC STRENGTH= 6.2296730E-01

FIXED PH= 8.000 COMPUTED TOTH= 0.1774696E 00

PCO2= 0.3194776E-03

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	4.8976541E-03	2.31001	1.0000002E-01	1.00000	0.0
MG	4.9781822E-02	1.30293	5.0118871E-02	1.30000	2.2828317E-08
NA	5.0115186E-01	0.30003	5.0118738E-01	0.30000	-4.4325134E-08
FE3	1.2589660E-20	19.89999	1.0000009E-02	2.00000	0.0
CO3-	2.0418025E-05	4.68999	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	4.0037377E-20

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.5073104E-02
FE3	OH	1	1.0000009E-02
H	CO3-	1	1.0316283E-01

9f.

PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN; BOUND SIGNIFIES COMPLEXED

CA

AS A FREE METAL/ 4.9 PERCENT
IN SOLID FORM WITH CO3-/ 95.1 PERCENT

MG

AS A FREE METAL/ 99.3 PERCENT
BOUND WITH CO3-/ 0.6 PERCENT

NA

AS A FREE METAL/ 100.0 PERCENT.

FE3

IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-

IN SOLID FORM WITH CA / 47.6 PERCENT
IN SOLID FORM WITH H / 51.7 PERCENT

CL

AS A FREE LIGAND/ 100.0 PERCENT

9g.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID						COMPLEXES															
		1		2		3		1		2		3		4		5		6	
1	1	700	1 1 0	0 0 0 0		0 0 0 0		170	1 1 0	1038	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
1	3	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
1	99	-2237	1 0-2	0 0 0 0		0 0 0 0		-1260	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	1	410	1 1 0	0 0 0 0		0 0 0 0		190	1 1 0	1038	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	3	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	99	-1687	1 0-2	0 0 0 0		0 0 0 0		-1160	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	1	0	0 0 0	0 0 0 0		0 0 0 0		54	1 1 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	3	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	99	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
6	1	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
6	3	0	0 0 0	0 0 0 0		0 0 0 0		43	1 1 0	48	1 2 0	-62	1 3 0	0 0 0 0		0 0 0 0		0 0 0 0	
6	99	-410	1 0-3	0 0 0 0		0 0 0 0		-291	1 0-1	-732	1 0-2	-2415	1 0-4	-305	2 0-2	0 0 0 0		0 0 0 0	
50	1	2069	0 1 2	0 0 0 0		0 0 0 0		963	0 1 1	1568	0 1 2	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
50	3	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
50	99	0	0 0 0	0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	

9h.
CASE NUMBER 3

CASE PROGRESS

NUMBER OF ITERATIONS= 28

SOLID CA CO3- 1 DISSOLVES

NUMBER OF ITERATIONS= 32

NUMBER OF ITERATIONS= 33

IONIC STRENGTH= 8.1328493E-01

FIXED PH= 4.000 COMPUTED TOTH= 0.3691529E 00

PCO2= 0.3214697E-03

9i.
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN; BOUND SIGNIFIES COMPLEXED

CA
AS A FREE METAL/ 100.0 PERCENT

MG
AS A FREE METAL/ 100.0 PERCENT

NA
AS A FREE METAL/ 100.0 PERCENT

FE3
IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-
IN SOLID FORM WITH H / 100.0 PERCENT

CL
AS A FREE LIGAND/ 100.0 PERCENT

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	9.9999964E-02	1.00000	1.0000002E-01	1.00000	-1.0367774E-08
MG	5.0118845E-02	1.30000	5.0118871E-02	1.30000	-2.4051894E-10
NA	5.0118738E-01	0.30000	5.0118738E-01	0.30000	3.5482202E-13
FE3	1.2022745E-08	7.92000	1.0000009E-02	2.00000	0.0
CO3-	1.9952974E-13	12.70000	1.9952637E-01	0.70000	0.0
CL	5.2480751E-01	0.28000	5.2480757E-01	0.28000	-1.9912246E-08

SOLID			MOLES PER LITER OF SOLUTION
FE3	OH	1	9.9997409E-03
H	CO3-	1	1.9951636E-01

Figure 10
A case with no solids allowed to precipitate

10a. Input cards

```
(1)   5  3  1 -1  0  0  1  0  0  1
(2) 1.11E 0
(3)  1    1.0    1.0
     2    1.3    1.3
     5    0.3    0.3
     6    2.0    2.0
(4)  1    1.0     0.7
     3    0.28   0.28
(5)       8.0
(6) 0.1
(7)  0.0
```

10b.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID						COMPLEXES															
		1		2		3		1		2		3		4		5		6	
1	1	0 0 0 0		0 0 0 0		0 0 0 0		181	1 1 0	1048	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
1	3	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
1	99	0 0 0 0		0 0 0 0		0 0 0 0		-1257	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	1	0 0 0 0		0 0 0 0		0 0 0 0		201	1 1 0	1048	1 1 1	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	3	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
2	99	0 0 0 0		0 0 0 0		0 0 0 0		-1157	1 0-1	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	1	0 0 0 0		0 0 0 0		0 0 0 0		60	1 1 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	3	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
5	99	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
6	1	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0 0 0 0		0 0 0 0		0 0 0 0		0 0 0 0	
6	3	0 0 0 0		0 0 0 0		0 0 0 0		51	1 1 0	61	1 2 0	-47	1 3 0	0 0 0 0		0 0 0 0		0 0 0 0	
6	99	0 0 0 0		0 0 0 0		0 0 0 0		-286	1 0-1	-723	1 0-2	-2408	1 0-4	-304	2 0-2	0 0 0 0		0 0 0 0	
50	1	0 0 0 0		0 0 0 0		0 0 0 0		968	0 1 1	1575	0 1 2	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0
50	3	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0
50	99	0 0 0 0		0 0 0 0		0 0 0 0		0	0 0 0	0	0 0 0	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0	0	0 0 0 0

10c.
CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 36

NUMBER OF ITERATIONS= 39

NUMBER OF ITERATIONS= 41

IONIC STRENGTH= 7.4154127E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 8.619

10d.
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN: BOUND SIGNIFIES COMPLEXED

CA		
	AS A FREE METAL/	49.7 PERCENT
	BOUND WITH CO3-/	50.3 PERCENT
MG		
	AS A FREE METAL/	43.6 PERCENT
	BOUND WITH CO3-/	56.3 PERCENT
NA		
	AS A FREE METAL/	96.8 PERCENT
	BOUND WITH CO3-/	3.2 PERCENT
FE3		
	BOUND WITH OH /	100.0 PERCENT
CO3-		
	AS A FREE LIGAND/	4.7 PERCENT
	BOUND WITH CA /	25.2 PERCENT
	BOUND WITH MG /	14.2 PERCENT
	BOUND WITH NA /	8.0 PERCENT
	BOUND WITH H /	48.0 PERCENT
CL		
	AS A FREE LIGAND/	100.0 PERCENT

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	4.9670812E-02	1.30390	1.0000002E-01	1.00000	-2.6781890E-08
MG	2.1857675E-02	1.66040	5.0118871E-02	1.30000	-1.6822014E-08
NA	4.8519003E-01	0.31409	5.0118738E-01	0.30000	-4.4703484E-08
FE3	3.3079458E-13	12.48044	1.0000009E-02	2.00000	-9.6823101E-08
CO3-	9.2925243E-03	2.03187	1.9952637E-01	0.70000	-8.7311491E-08
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	1.0535964E-12
TOTH	2.4070772E-09	8.61851	9.9999964E-02		4.8102811E-07

Figure 11
A case with 1 solid not allowed and 1 solid imposed

11a. Input cards

```
(1)   5  3  1  2  0  0  1  0  0  1
(2) 1.11E 0
(3)  1    1.0    1.0
     2    1.3    1.3
     5    0.3    0.3
     6    2.0    2.0
(4)  1    1.0     0.7
     3    0.28   0.28
(5)       8.0
(6) 0.1
(7)  0.0
(10) 0101-10201 1
```


11b.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID 1	SOLID 2	SOLID 3	COMPLEXES 1	COMPLEXES 2	COMPLEXES 3	COMPLEXES 4	COMPLEXES 5	COMPLEXES 6
1	1	0 0 0 0	0 0 0 0	0 0 0 0	181 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	99	-2234 1 0-2	0 0 0 0	0 0 0 0	-1257 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	1	421 1 1 0	0 0 0 0	0 0 0 0	201 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	99	-1684 1 0-2	0 0 0 0	0 0 0 0	-1157 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	1	0 0 0 0	0 0 0 0	0 0 0 0	60 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	3	0 0 0 0	0 0 0 0	0 0 0 0	51 1 1 0	61 1 2 0	-47 1 3 0	0 0 0 0	0 0 0 0	0 0 0 0
6	99	-401 1 0-3	0 0 0 0	0 0 0 0	-286 1 0-1	-723 1 0-2	-2408 1 0-4	-304 2 0-2	0 0 0 0	0 0 0 0
50	1	-4 0 1 2	0 0 0 0	0 0 0 0	968 0 1 1	1575 0 1 2	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0

11c.

INPUT DATA

THESE COMPUTATIONS INVOLVE 5 METALS, 3 LIGANDS, 16 COMPLEXES AND 5 POSSIBLE SOLIDS.

IONIC STRENGTH= 0.1110000E 01

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	TOTCC
CA	1	1.000	1.000	
MG	2	1.300	1.300	
NA	5	0.300	0.300	
FE3	6	2.000	2.000	
LIGAND	#INMAT	GUESS	TOTCC 1	TOTCC
CO3-	1	1.000	0.700	
CL	3	0.280	0.280	
PH GUESS	1	8.000		
TOTH			0.10E 00	

THE FOLLOWING 1 SOLIDS ARE IMPOSED AT THE START OF THE COMPUTATION

METAL	LIGAND	
MG	CO3-	1

11d.

CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 31

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 34

NUMBER OF ITERATIONS= 37

NUMBER OF ITERATIONS= 38

IONIC STRENGTH= 7.2026575E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 8.486

11e.

PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN: BOUND SIGNIFIES COMPLEXED

CA
AS A FREE METAL/ 53.1 PERCENT
BOUND WITH CO3-/ 46.9 PERCENT

MG
AS A FREE METAL/ 22.7 PERCENT
BOUND WITH CO3-/ 24.7 PERCENT
IN SOLID FORM WITH CO3-/ 52.5 PERCENT

NA
AS A FREE METAL/ 97.6 PERCENT
BOUND WITH CO3-/ 2.4 PERCENT

FE3
IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-
AS A FREE LIGAND/ 3.4 PERCENT
BOUND WITH CA / 23.5 PERCENT
BOUND WITH MG / 6.2 PERCENT
IN SOLID FORM WITH MG / 13.2 PERCENT
BOUND WITH NA / 5.9 PERCENT
BOUND WITH H / 47.7 PERCENT

CL
AS A FREE LIGAND/ 100.0 PERCENT

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	5.3096782E-02	1.27493	1.0000002E-01	1.00000	1.0258900E-06
MG	1.1388279E-02	1.94354	5.0118871E-02	1.30000	-3.8519502E-06
NA	4.8935264E-01	0.31038	5.0118738E-01	0.30000	1.5646219E-07
FE3	4.2789875E-22	21.36867	1.0000009E-02	2.00000	0.0
CO3-	6.8162009E-03	2.16646	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	1.3628932E-21
TOTH	3.2641161E-09	8.48623	9.9999964E-02		3.3192337E-06

SOLID			MOLES PER LITER OF SOLUTION
MG	CO3-	1	2.6330061E-02
FE3	OH	1	1.0000009E-02

Figure 12
Four redox cases from oxidizing to reducing

12a. Input cards

```
(1)   6  3  4  0  0  0  1  1  0  1
(2) 1.11E 0
(3)  1    1.0    1.0
     2    1.3    1.3
     5    0.3    0.3
     6    2.0    2.0
     7    8.0    8.0
(4)  1    1.0     0.7
     3    0.28   0.28
(5)       8.0
(6)   0.1    0.1    0.1    0.1
(7)  0.0
(8)  12.0   8.0   0.0 -4.0
(11) 01
```


12b.
INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID 1	SOLID 2	SOLID 3	COMPLEXES 1	COMPLEXES 2	COMPLEXES 3	COMPLEXES 4	COMPLEXES 5	COMPLEXES 6
1	1	711 1 1 0	0 0 0 0	0 0 0 0	181 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	99	-2234 1 0-2	0 0 0 0	0 0 0 0	-1257 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	1	421 1 1 0	0 0 0 0	0 0 0 0	201 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	99	-1684 1 0-2	0 0 0 0	0 0 0 0	-1157 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	1	0 0 0 0	0 0 0 0	0 0 0 0	60 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	3	0 0 0 0	0 0 0 0	0 0 0 0	51 1 1 0	61 1 2 0	-47 1 3 0	0 0 0 0	0 0 0 0	0 0 0 0
6	99	-401 1 0-3	0 0 0 0	0 0 0 0	-286 1 0-1	-723 1 0-2	-2408 1 0-4	-304 2 0-2	0 0 0 0	0 0 0 0
7	1	901 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
7	3	0 0 0 0	0 0 0 0	0 0 0 0	30 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
7	99	-1314 1 0-2	0 0 0 0	0 0 0 0	-897 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	1	-4 0 1 2	0 0 0 0	0 0 0 0	968 0 1 1	1575 0 1 2	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0

REDOX DATA	KRED	MREDOX	LREDOX	NELEC	NMRED	REDCST

12c.

INPUT DATA

THESE COMPUTATIONS INVOLVE 6 METALS, 3 LIGANDS, 18 COMPLEXES AND 8 POSSIBLE SOLIDS.

IONIC STRENGTH= 0.1110000E 01

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

4 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	TOTCC 2	TOTCC 3	TOTCC 4	TOTCC
CA	1	1.000	1.000	1.000	1.000	1.000	
MG	2	1.300	1.300	1.300	1.300	1.300	
NA	5	0.300	0.300	0.300	0.300	0.300	
FE3	6	2.000	2.000	2.000	2.000	2.000	
FE2	7	8.000	8.000	8.000	8.000	8.000	
LIGAND	#INMAT	GUESS	TOTCC 1	TOTCC 2	TOTCC 3	TOTCC 4	TOTCC
CO3-	1	1.000	0.700	0.700	0.700	0.700	
CL	3	0.280	0.280	0.280	0.280	0.280	
PH GUESS 1		8.000					
TOTH			0.10E 00	0.10E 00	0.10E 00	0.10E 00	
REDOX POTENTIAL			12.000	8.000	0.0	-4.000	

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED
FE2/FE3

12d.

CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 37

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 40

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 49

NUMBER OF ITERATIONS= 52

IONIC STRENGTH= 6.3052249E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.410

PE= 12.00

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	2.6781587E-03	2.57216	1.0000002E-01	1.00000	-1.2636185E-05
MG	3.7081730E-02	1.43084	5.0118871E-02	1.30000	1.4984471E-06
NA	5.0112247E-01	0.30006	5.0118738E-01	0.30000	-2.9700459E-08
FE3	7.4247097E-16	15.12932	1.0000017E-02	2.00000	2.1515789E-15
FE2	1.1237857E-15	14.94933	0.0	********	2.1515789E-15
CO3-	3.7339152E-05	4.42784	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	3.3860445E-15
TOTH	3.8924406E-07	6.40978	9.9999964E-02		1.6041100E-05

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.6370399E-02
FE3	OH	1	1.0000013E-02

12e.

CASE NUMBER 2

CASE PROGRESS

NUMBER OF ITERATIONS= 60

IONIC STRENGTH= 6.3051867E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.410

PE= 8.00

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	2.6784043E-03	2.57212	1.0000002E-01	1.00000	0.0
MG	3.7081737E-02	1.43084	5.0118871E-02	1.30000	1.5787066E-08
NA	5.0112247E-01	0.30006	5.0118738E-01	0.30000	-3.5695848E-08
FE3	7.4242565E-16	15.12936	1.0000017E-02	2.00000	2.1514179E-11
FE2	1.1237022E-11	10.94936	0.0	********	2.1514179E-11
CO3-	3.7335747E-05	4.42788	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	1.0250661E-11
TOTH	3.8923531E-07	6.40979	9.9999964E-02		1.1175871E-08

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.6382797E-02
FE3	OH	1	1.0000013E-02

12f.

CASE NUMBER 3

CASE PROGRESS

NUMBER OF ITERATIONS= 67

SOLID FE2 CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 81

SOLID FE3 OH 1 DISSOLVES

NUMBER OF ITERATIONS= 85

IONIC STRENGTH= 6.2756062E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.875

PE= 0.0

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	8.5869664E-04	3.06616	1.0000002E-01	1.00000	-1.7881393E-07
MG	3.6262427E-02	1.44054	5.0118871E-02	1.30000	3.0554190E-08
NA	5.0098509E-01	0.30018	5.0118738E-01	0.30000	-2.6921043E-09
FE3	7.1426095E-18	17.14615	1.0000017E-02	2.00000	-3.7252903E-09
FE2	1.0810385E-05	4.96616	0.0	********	-3.7252903E-09
CO3-	1.1645581E-04	3.93384	1.9952637E-01	0.70000	-4.4703484E-08
CL	5.2479768E-01	0.28001	5.2480757E-01	0.28000	-3.5329322E-08
TOTH	1.3346596E-07	6.87463	9.9999964E-02		1.1920929E-07

SOLID	MOLES PER LITER OF SOLUTION
CA CO3- 1	9.8815858E-02
FE2 CO3- 1	9.9792629E-03

12g.

CASE NUMBER 4

CASE PROGRESS

NUMBER OF ITERATIONS= 93

IONIC STRENGTH= 6.2756062E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.875

PE= -4.00

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	8.5870270E-04	3.06616	1.0000002E-01	1.00000	-2.9802322E-07
MG	3.6262434E-02	1.44054	5.0118871E-02	1.30000	3.8000223E-08
NA	5.0098509E-01	0.30018	5.0118738E-01	0.30000	-3.8417056E-09
FE3	7.1429227E-22	21.14613	1.0000017E-02	2.00000	-3.7252903E-09
FE2	1.0810458E-05	4.96616	0.0	********	-3.7252903E-09
CO3-	1.1645503E-04	3.93384	1.9952637E-01	0.70000	-4.4703484E-08
CL	5.2479768E-01	0.28001	5.2480757E-01	0.28000	-3.5262929E-08
TOTH	1.3346687E-07	6.87463	9.9999964E-02		2.4586916E-07

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	9.8815739E-02
FE2	CO3-	1	9.9792629E-03

Figure 13
A case with one mixed solid allowed

13a. Input cards

```
(1)   5  3  1  0  0  0  1  0  1  1
(2) 1.11E 0
(3)  1    1.0    1.0
     2    1.3    1.3
     5    0.3    0.3
     6    2.0    2.0
(4)  1    1.0     0.7
     3    0.28   0.28
(5)       8.0
(6) 0.1
(7)  0.0
(12)        -2   -3   -4    -6
```


13b.
INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH LAST USED

MET	LIG	SOLID 1	SOLID 2	SOLID 3	COMPLEXES 1	COMPLEXES 2	COMPLEXES 3	COMPLEXES 4	COMPLEXES 5	COMPLEXES 6
1	1	711 1 1 0	0 0 0 0	0 0 0 0	181 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
1	99	-2234 1 0-2	0 0 0 0	0 0 0 0	-1257 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	1	421 1 1 0	0 0 0 0	0 0 0 0	201 1 1 0	1048 1 1 1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
2	99	-1684 1 0-2	0 0 0 0	0 0 0 0	-1157 1 0-1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	1	0 0 0 0	0 0 0 0	0 0 0 0	60 1 1 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
5	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	1	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
6	3	0 0 0 0	0 0 0 0	0 0 0 0	51 1 1 0	61 1 2 0	-47 1 3 0	0 0 0 0	0 0 0 0	0 0 0 0
6	99	-401 1 0-3	0 0 0 0	0 0 0 0	-286 1 0-1	-723 1 0-2	-2408 1 0-4	-304 2 0-2	0 0 0 0	0 0 0 0
50	1	-4 0 1 2	0 0 0 0	0 0 0 0	968 0 1 1	1575 0 1 2	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	3	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0
50	99	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0

MIXED SOLIDS DATA

5 IM(1)_ IM(2)_ 2L(1)_ 0L(99)_ 0H CONSTANT= 173

13c.
CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 36

MIXED SOLID # 5 PRCPIATES: CA MG CO3- OH

NUMBER OF ITERATIONS= 47

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 52

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 57

NUMBER OF ITERATIONS= 60

IONIC STRENGTH= 5.8201408E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 5.777

13d.
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.05% SHOWN: BOUND SIGNIFIES COMPLEXED

CA
AS A FREE METAL/ 26.8 PERCENT
BOUND WITH CO3-/ 4.0 PERCENT
IN SOLID FORM WITH CO3-/ 19.1 PERCENT
IN SOLID FORM IN MIXED SOLID# 5/ 50.1 PERCENT

MG
IN SOLID FORM IN MIXED SOLID# 5/ 99.9 PERCENT

NA
AS A FREE METAL/ 100.0 PERCENT

FE3
IN SOLID FORM WITH OH / 100.0 PERCENT

CO3-
BOUND WITH CA / 2.0 PERCENT
IN SOLID FORM WITH CA / 9.6 PERCENT
BOUND WITH H / 38.2 PERCENT
IN SOLID FORM IN MIXED SOLID# 5/ 50.2 PERCENT

CL
AS A FREE LIGAND/ 100.0 PERCENT

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	2.6840061E-02	1.57122	1.0000002E-01	1.00000	-5.7369471E-07
MG	2.6840120E-05	4.57122	5.0118871E-02	1.30000	0.0
NA	5.0118089E-01	0.30001	5.0118738E-01	0.30000	-2.2308996E-08
FE3	5.8620209E-14	13.23196	1.0000009E-02	2.00000	0.0
CO3-	3.7257860E-06	5.42878	1.9952637E-01	0.70000	0.0
CL	5.2480757E-01	0.28000	5.2480757E-01	0.28000	1.8641832E-13
TOTH	1.6698559E-06	5.77732	9.9999964E-02		1.1473894E-06

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	1.9060493E-02
FE3	OH	1	1.0000005E-02

MIXED SOLID	MOLES PER LITRE OF SOLUTION
5 CA MG CO3- OH	5.0088011E-02

Figure 14
A case with milligram/liter input

14b.

INPUT DATA

THESE COMPUTATIONS INVOLVE 5 METALS, 3 LIGANDS, 16 COMPLEXES AND 6 POSSIBLE SOLIDS.

IONIC STRENGTH= 0.1110000E 01

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	TOTCC
CA	1	.401E 04	.401E 04	
MG	2	.122E 04	.122E 04	
NA	5	.115E 05	.115E 05	
FE3	6	.559E 03	.559E 03	
LIGAND	#INMAT	GUESS	TOTCC 1	TOTCC
CO3-	1	.600E 04	.120E 05	
CL	3	.188E 05	.188E 05	
PH GUESS 1		8.000		
TOTH			0.10E 00	

14a. Input cards

```
(1)   5  3  1              1         1                    1
(2) 1.11E 0
(3) 01  401E 3401E 3
    02  122E 3122E 3
    05  115E 4115E 4
    06  559E 2559E 2
(4) 01   60E 4120E 4
    03  188E 4188E 4
(5)       8.0
(6)   0.1
(7) 0.0
```

14c.
CASE NUMBER 1

CASE PROGRESS

NUMBER OF ITERATIONS= 37

SOLID FE3 OH 1 PRECIPITATES

NUMBER OF ITERATIONS= 40

SOLID CA CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS= 48

NUMBER OF ITERATIONS= 51

IONIC STRENGTH= 6.3380075E-01

FIXED TOTH= 0.9999996E-01 COMPUTED PH= 6.287

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
	MG/L		MG/L		
CA	1.6256105E 02	-2.21102	4.0100029E 03	-3.60314	-3.0339694E-01
MG	9.3337964E 02	-2.97006	1.2200020E 03	-3.08636	2.0031713E-02
NA	1.1499016E 04	-4.06066	1.1500000E 04	-4.06070	-8.3871256E-04
FE3	9.6560884E-11	10.01519	5.5900098E 02	-2.74741	0.0
CO3-	1.5288792E 00	-0.18437	1.2000004E 04	-4.07918	0.0
CL	1.8800000E 04	-4.27416	1.8800000E 04	-4.27416	1.9816851E-10
TOTH	5.1592599E-07	6.28741	9.9999964E-02		1.0203570E-05

SOLID			MG PER LITER OF SOLUTION
CA	CO3-	1	9.6723945E 03
FE3	OH	1	1.0696985E 03

Figure 15

INTERACTION CAPACITIES:

	CA	MG	K	NA	FE3	FE2	MN	AL	CO3-
CA	-9.18E+03	-1.95E+02	-2.99E-04	-7.96E-01	-2.45E+04	-2.45E+04	-7.66E+02	-2.28E+04	7.63E+03
MG	-1.95E+02	-9.95E+03	-8.56E-03	-2.19E-02	-4.33E+02	-4.33E+02	-1.67E+01	-4.03E+02	1.77E+02
K	-2.99E-04	-8.56E-03	-1.07E+04	-1.99E-04	-7.24E-04	-7.24E-04	-6.18E-03	-6.74E-04	2.63E-04
NA	-7.96E-01	-2.19E-02	-1.99E-04	-1.69E+03	-2.95E+00	-2.95E+00	-7.04E-02	-2.74E+00	1.31E+00
FE3	-2.45E+04	-4.33E+02	-7.24E-04	-2.95E+00	-9.08E+04	-9.08E+04	-2.01E+03	-8.45E+04	2.83E+04
FE2	-2.45E+04	-4.33E+02	-7.24E-04	-2.95E+00	-9.08E+04	-9.08E+04	-2.01E+03	-8.45E+04	2.83E+04
MN	-7.66E+02	-1.67E+01	-6.18E-03	-7.04E-02	-2.01E+03	-2.01E+03	-2.68E+05	-1.87E+03	6.52E+02
AL	-2.28E+04	-4.03E+02	-6.74E-04	-2.74E+00	-8.45E+04	-8.45E+04	-1.87E+03	-8.18E+04	2.63E+04
CO3-	7.63E+03	1.77E+02	2.63E-04	1.31E+00	2.83E+04	2.83E+04	6.52E+02	2.63E+04	-1.26E+04
SO4	2.89E+00	8.26E+01	4.82E+00	1.92E+00	6.99E+00	6.99E+00	5.96E+01	6.51E+00	-2.54E+00
CL	1.21E-02	2.66E-04	9.80E-08	1.12E-06	3.19E-02	3.19E-02	4.25E+00	2.97E-02	-1.03E-02
PO4	1.26E+04	2.76E+02	4.19E-04	9.98E-01	3.08E+04	3.08E+04	1.05E+03	2.86E+04	-9.57E+03
SIO3	1.46E+04	2.59E+02	4.33E-04	1.76E+00	5.43E+04	5.43E+04	1.20E+03	5.36E+04	-1.69E+04
H	-8.17E+03	-1.44E+02	-2.41E-04	-9.83E-01	-3.03E+04	-3.03E+04	-6.71E+02	-2.82E+04	9.42E+03

Figure 16
A nonconvergent case

CASE NUMBER 3

NUMBER OF ITERATIONS= 38

SOLID FE3 OH 1 PRECIPITATES

****

BE CAREFUL NO CONVERGENCE

****

SOLID FE2 CO3- 1 DISSOLVES

IONIC STRENGTH= 6.2702394E-01

FIXED TOTH= 0.1000000E+00 COMPUTED PH= 3.051

PE= 8.00

	FREE CONC	-LOG FREE CONC	TOT CONC	-LOG TOT CONC	REMAINDER
CA	1.0880752E+01	-1.03666	1.0000002E-01	1.00000	0.0
MG	4.1905552E-02	1.37773	5.0118778E-02	1.30000	-1.4779989E-08
NA	5.0118726E-01	0.30000	5.0118732E-01	0.30000	-4.3632799E-08
FE3	8.8442575E-06	5.05334	1.0000017E-02	2.00000	2.4635345E+01
FE2	1.3698083E-01	0.86334	0.0	********	2.4635345E+01
CO3-	9.1909129E-09	8.03665	1.9952637E-01	0.70000	2.4635345E+01
CL	4.2388415E-01	0.37275	5.2480757E-01	0.28000	2.3841858E-07
TOTH	8.8896835E-04	3.05111	1.0000002E-01		1.3732910E-04

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	-1.2913297E+01
FE3	OH	1	2.4407425E+01